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MATERIAL ENGINEERING
AND AVIATION STRUCTURAL MATERIALS

Part 2

NON-METALS AND COMPOSITES

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Textbook

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Посібник є другою частиною курсу лекцій "Авіаційне матеріалознавство", що спрямований на вивчення узагальненого підходу щодо вибору конструкційних матеріалів для силових елементів авіаційних конструкцій, методів випробувань матеріалів, оцінювання механічних властивостей, основних шляхів зміцнювання конструкційних матеріалів. Увагу приділено сучасним конструкційним полімерам, гумам спеціального призначення, композиційним матеріалам, кераміці, сіталам, склу та допоміжним конструкційним матеріалам – клеям, захисним покриттям, герметикам. Розглянуто також основні технологічні процеси перероблення у вироби неметалевих конструкційних матеріалів.

Для студентів, що вивчають курс "Авіаційне матеріалознавство".

This textbook is the second part of "Aviation Materials" lecture course which is directed to studying generalized approach of selection structural materials for aviation structures, material testing methods, estimation of mechanical properties, main ways of structural material strengthening. In the textbook such non-metal structural materials as polymers, rubbers for special application, composites, ceramics, glass-ceramic materials, glasses and auxiliary structural materials – adhesives, protective coatings, sealants are considered. Main methods of above-mentioned materials processing to final articles are observed too.

For students studying course "Aviation materials".

CONTENTS

Introduction

One of the most valuable ability of an up-to-date successful mechanical engineer is feeling of structural material development directions and possession of knowledge about physical-mechanical fundamentals of structural materials. Fist of all main requirements to advanced structural materials are high-specific properties at practical economical availability and cost because these characteristics permit to realize practically aviation and aerospace structures with necessary reliability, quality and customer demands.

Appearing of a new structural material, technologies, re-sharing of world markets of raw materials and influence of social life requires continuous observation of material engineering science applied side. Conventional materials can't satisfy such strong design, manufacturing, operational and service restrictions of aerospace technique as minimal allowable safety factors, aerodynamic and radiation heating, short manufacturing cycle and lifetime at minimal cost, modular arrangement of aircrafts, simplified access to internal units. Nowadays special steels, aluminium, titanium, copper, nickel, lithium, beryllium alloys, high-temperature and heat-resistant materials are widely used in aerospace objects. Moreover a large variety of non-metal structural materials (glasses, ceramics, glass-ceramics, composites) are used for making aircraft main load-carrying elements.

The main objective of this book is to help a reader to arrange and classify structural materials, graduate levels of physical and mechanical properties, designate main milestones of structural material development and create consequent algorithm of selection structural material for exact application at known restrictions. Information gathered in this notes was drawn from series of published scientific articles, results of fundamentals studies conducted by well-known machine-building and aviation enterprises of Ukraine and other countries.

For more deep analysis of definite question the list of literature used and appendixes containing information about mostly used ceramics, glass-ceramics, composites, adhesives are shown at the end of this textbook. More specific info (for example, some numerical values) one has to seek in correspondent reference and guide books.

Theme 1. THERMOPLASTICS AND THERMOSETTING STRUCTURAL MATERIALS

The artificial materials, obtained from organic polymerizable binders, are called plastics. They are capable during the heating of being softened, of becoming plastic and of gaining the prescribed form under the applied pressure. With respect to the heating polymeric materials are subdivided into the **thermoplastic** and the **thermosetting**. Thermoplastic polymers during the heating are softened, melt, and during the cooling they become hard. Moreover, this process is reversible. Thermosetting polymers during the heating are softened, as a result of the irreversible chemical reactions they harden and remain solid subsequently. Then hardened (cured) state of polymer remains thermostable.

Thermoplastic structural materials

Polymers of the linear or branched structure are the basis of thermoplastic plastics. Sometimes plasticizers are introduced into the composition of polymers. Thermoplastics have limited operating temperature. At the temperatures more than 60…70℃ sharp reduction in the phys ical-mechanical properties begins. There are more heat-resistant structures, which can work at temperatures to 400…600℃.

With the prolonged static loading elastic deformation appears and strength is reduced. The crystal polymers are more strong and more rigid. The ultimate strength of thermoplastics is 10…100 MPa. The elasticity modulus is 1.8…3.5 GPa. They resist fatigue well; their service life is higher than life of the metals. Endurance limit is about 0.2…0.3 of ultimate strength. Thermoplastics are divided into the non-polar and the polar.

Non-polar thermoplastic plastics

They include polyethylene, polypropylene, polystyrene and teflon-4. **Polyethylene** is the product of the polymerization of ethylene. According to the density polyethylene is subdivided into the low-density polyethylene, obtained in the polymerization at a high pressure, and the high-density polyethylene, obtained at a low pressure. Polyethylene is chemically stable and at a normal temperature is not dissolved in the known solvents. A drawback in polyethylene is its susceptibility to aging. Polyethylene is used for manufacturing of pipes, casting and pressed non-load-bearing parts, films; it is used as coating on metals for corrosion protection, moisture and electric current.

Polypropylene is the derivative of ethylene. This plastic is more heat-resistant in comparison with polyethylene: its structure is stable up to the temperature of 150℃. Polypropylene is more gas-imperm eable, filaments are elastic, strong and it is chemically stable. The drawback of propylene is its low frost

resistance - from -10 to -20℃. It is used for manu facturing pipes, structural parts, pump casings, different capacities.

Polystyrene is solid, rigid, transparent, amorphous polymer. It is convenient for machining, it is painted well, and soluble in the benzene. Polystyrene is most stable to the effect of the ionizing emission in comparison with other thermoplastics. Drawbacks in the polystyrene are: low thermal stability, tendency to aging, crack formation. It is possesses the increased chemical stability and light-thermal stability. The parts for radio engineering, tools, machine part, the containers for the water and the chemicals, the film for the electro-insulation, the parts of vehicles, boats, and pipes are manufactured from the polystyrene.

Teflon-4 can operate for a long time up to the 250℃ and at low temperatures the plastic doesn't become brittle. Teflon-4 has high resistance to the action of solvents, acids, alkalies, oxidizers. This plastic is not wet by water. Teflon-4 is used for manufacturing of pipes, valves, pumps, diaphragms, sealing gaskets, sealing ring, silphons, electro- and radio engineering parts, antifriction coatings on the metals (bearings, bushes). Some properties of thermoplastics are given in Table 1.1.

Polar thermoplastic materials

The polar plastics include teflon-3, organic glass, the polyvinyl chloride, polyamides, polyurethanes, polycarbonate, pentaplast, polyformaldehyde.

Teflon-3 has high resistance to acids, oxidizers, solutions of alkalis and organic solvents. Teflon-3 is used as a low-frequency dielectric for manufacturing pipes, hoses, valves, pumps, protective coatings of metals, etc.

Organic glass (plexiglass or PMMC) is the transparent amorphous thermoplastics on the basis of ethers and acids. It is characterized by high weather resistance, it is optically transparent (light transparency up to 92 %), transmitting 75 % ultraviolet radiation. Organic glass begins to be softened at a temperature 80℃; at a temperature 105…150℃ the plast icity appears, which makes it possible to mold different parts from it. Organic glass is stable to the action of dilute acids and alkalis, hydrocarbon fuels and lubricants. Aging organic glass under the natural conditions flows slowly. Low surface hardness is a drawback in the organic glass. Organic glass is utilized in the aircraft construction, the automobile construction. Illuminating engineering parts, optical lenses, dies, casting patterns are manufactured from it.

Polyvinyl chloride (PVC) is amorphous polymer. It has good electrical insulating characteristics, is steady to the chemicals, is not supported combustion. This polymer is weatherproof. Solid polyvinyl chloride without the plasticizer is called polyvinyl chloride plastic. Polyvinyl chloride plastic has a high strength and elasticity. Pipes, parts of ventilation installations and heat exchangers, protective coatings for the metallic capacitances, construction facing plates are manufactured from PVC

Table 1.1. Physical-mechanical properties of thermoplastic materials

Material	Density, g/cm^3	Operating temperature, °C		Ultimate strength, MPa			Elongation at rupture, %	Modulus of elasticity, GPa
		мax	мin	at tension	at compression	In bending		
Teflon-3	2.9…2.16	125	-195	30...45	50...80	60...80	20...200	2.2...3.3
Organic glass	1.2	60	-60	63...100	100...105	90...120	2.5...20	2.9...4.16
Polyvinylchloride	1.4	65…80	-10…-40	40...120	80...160	40...120	5...100	2.6...3.0
Polyamide	1.1…1.14	60…110	-20…-60	38...60	70...120	35...70	70...280	1.2...1.5
Polycarbonate	1.2	130…140	-100…-135	70	90...110	24...120	120...180	1.3...1.9
Polyacrylate	1.2	155…250	-100	55...120.	105...145	100...125	15...20	1.65
Pentaplast	1.4	150	-20	80...110	90...100	80...100	5...10	1.5
Polyformaldehyde stabilized	1.14…1.4	130	-40…-60	20...55	85...95	60...85	10...40	1.3
High density PVC	0.913…0.929	105…108	-80	10...17	12	12...17	50...600	1.8...3.5
Low density PVC	0.949…0.953	120…125	-80	18...35	20...36	20...36	250...1000	
Polypropylene	0.9	150	-15	25...40	11	11	200...800	
Polystyrene	1.05…1.08	90	-20	37...48	90...100	90...100	1...4	
Teflon-4	1.9…2.2	250	-269	15...35	10…12	10...12	250...500	

plastics. Drawbacks in this material are low stress-rupture strength and low operating temperature, high coefficient of linear expansion, brittleness at low temperatures (less than -10℃).

Representatives of **Polyamides** group are capron, nylon, etc. They have the low coefficient of friction ($f < 0.05$); can work prolonged time on the abrasion; furthermore, they have high impact toughness and capable of absorbing vibration, stable to the alkali, gasoline, alcohol, and resistant to the tropical climate. Hygroscopicity and susceptibility to aging are the main drawbacks of polyamides. Gears, inserts, bearings, bolts, nuts, blocks are manufactured from polyamides. Polyamides are also used as antifriction coatings of metals.

Polyurethanes. They are flexible and elastic; high weather resistance and frost resistance are inherent to them. The properties of polyurethane in general are close to the properties of polyamides. From polyurethane the film materials and the filaments which are slightly hygroscopic and chemically stable are manufactured.

Polycarbonate. By the properties it is close to PVC plastic and is characterized by high impact toughness and high strength at below zero temperatures. Polycarbonate is chemically stable to the solutions of salts, the dilute acids and the alkalies, oils; it is ruptured with strong alkalies; it resists light-heat-vacuum aging and thermal shocks, has the limited resistance to the effect of the ionizing emission. The gear, bearings, autos-part, radio parts are manufactured from polycarbonate. It is possible to utilize polycarbonate in cryogenics for the work in the medium of liquid gases.

Pentaplast. The strength of pentaplast is close to the strength of PVC plastic, it is molded well, has high water- and wear resistance. Pentaplast has satisfactory electrical insulating properties. The pipes, the valves, the parts of pumps and precision instruments, capacitances and protective coatings on the metals are manufactured from pentaplast.

Polyformaldehyde. It is water-resistant, resistant to mineral oils and gasoline; it is used for manufacturing of gear drives, gears, bearings, valves, parts of vehicles, conveyors etc.

Thermal-resistant plastics

Temperature of their operation is up to 400℃. Gene rally substances with cyclic molecular arrangement are stable to temperature of 600℃ and above. These plastics include: phenilon, polysulfone, polyimides, etc. Bearings, packing elements of locking devices, gears, parts of equipment, surgical tools, insulation on the high-frequency installations, parts, machine tools, everyday machines, and electrotechnical articles are manufactured from these materials.

Thermoplastics with the fillers

Different thermoplastics are used as polymeric bonding agents. As the reinforcing fillers it is possible to utilize a glass, basalt, carbon fibers, asbestos, organic filaments and fabrics. On an industrial scale polyamides and polycarbonates filled with the milled glass fibers are used. In comparison with the unfilled polymers the fiberglass materials have increased fatigue strength, wear resistance, and small creep. Thermoplastics generally are filled with the fillers in the form of synthetic fibers (propylene filament, capron, Lavsan - polyethylene therephthalate film (Dacron)). Laminated thermoplastics contain fabric from different filaments as the fillers. Polyamides, reinforced by fiberglass fabric, are used for obtaining the high-strength plastics. Bearings, gear drives, pipes, valves, capacitances for aggressive media are manufactured from the fibrous thermoplastics.

Thermosetting plastics

For manufacturing thermosetting plastics correspondent thermosetting resins (binders) are used. The main requirements for the binders are these: high pasting ability (adhesion), high thermal stability, chemical stability and electrical insulating properties, simplicity of manufacturing, small shrinkage and the lowest toxicity. It is necessary that the temperature coefficients of the linear expansion of bonding agent and filler would be close to each other.

In the production of plastics phenol-formaldehyde, silicon, epoxy resins, unlimited polyesters and their different modifications are widely implemented. Epoxy bonding agents have higher adhesion to the filler. These bonding agents make it possible to obtain the reinforced plastics with the high mechanical strength. Depending on the shape of the particles of the filler thermosetting plastics can be subdivided into the following groups: powder, fibrous and laminated.

Plastics with the powder fillers

Typical organic powder filler is sawdust and mineral one are milled quartz, asbestos, mica, graphite powders. The properties of powder plastics are characterized by isotropy, low mechanical strength and low impact toughness, satisfactory electrical insulating indices. They are used for the non-load-bearing structural and electrical insulating parts.

The mineral fillers give to a plastic high water resistance, chemical stability, good electrical insulating properties, and stability to the tropical climate. Compositions on the basis of epoxy resins are used widely in machine building for the manufacture of different tool equipment, exhaust and molding dies, housings of machine-tool, assembly and control fixtures and other equipment. They are used for the restoration of the worn parts and the cast.

Plastics with the fibrous fillers

This group of plastics includes continuous fiber-filled molding materials, asbestos fiber plastics, and fiberglass materials.

Fiber-filled molding materials are the compositions from the fibrous filler in the form of cotton tows, impregnated with phenol-formaldehyde bonding agent. In comparison with the molding powders they have increased strength and impact toughness. They are used for manufacturing parts of general technical purpose, working at bending and twisting (handles, struts, flanges, guide bushings, blocks, flywheels, etc).

Asbestos fiber plastics are based on asbestos fibers as the filler and phenol-formaldehyde resin serves as bonding agent. The advantage of asbestos fiber plastics is the increased thermal stability (more than 200°C), stability to the acid media and high frictional properties. Asbestos fiber plastics are used as the material of braking devices, acid-resistant apparatuses, baths, pipes.

Fiberglass materials is the composition, which consists of the synthetic resin (bonding agent), and fiberglass filler. Continuous or short fiberglass is used as the filler.

The disoriented fiberglass materials contain as the filler short filament. This makes it possible to form parts of variable shape, with the metal reinforcement. After molding the material has isotropic strength characteristics, considerably higher than molding powders and some fiber-filled molding materials possess.

The oriented fiberglass materials have filler in the form of the long (i.e. length-to-diameter ratio is more than 10) filaments, which are furnished oriented by separate strands and thoroughly cementing by bonding agent. This ensures the higher strength of glass-fiber-reinforced plastic.

Laminated plastics

Laminated plastics are load-bearing structural and building materials. The laminated fillers (laminas) packed by layers lead to plastic anisotropy. Materials are produced in the form of sheets, plates, pipes, blanks, from which different parts are obtained by machining. This group includes these materials: Getinax (i.e. laminated paper-Bakelite insulating material), Textolite (i.e. wood laminate plastics), asbestos-Textolite, fiberglass laminates, material CBAM – anisotropic glass fiber material.

Getinax is obtained on the basis of modified phenol, aniline-formaldehyde and carbamide resins and different types of paper. According to the further application Getinax is subdivided into the electro-technical and the decorative. It is resistant to the action of chemicals, solvents of the foodstuffs: it is utilized for the internal facing of passenger compartments of aircraft, railroad cars, cabins of vessels, in the building.

Textolite. Among the laminated plastic it possesses the best vibration absorption, highest strength (bonding agent - thermosetting resins, filler - cotton fabrics). Depending on application Textolites can be divided on the structural, electrotechnical, graphitized, and flexible packaging. They are used in rolling mills, the centrifugal pumps, the turbines.

Wooded laminate plastics (ДСП) consist of thin sheets of wood veneer, resin-impregnated and pressed in the form of sheets. From ДСП the blocks, inserts, sliders of gang saws, pump casings, bearings, parts of vehicles are manufactured.

Asbestos-textolite contains 38…43 % of bonding agent, rest is asbestos cloth. Asbestos-textolite is structural, frictional and thermo-insulating material. The blades of rotational fuel pumps, the clutch plates, the brake shoes are made of the asbestos-textolite. It is used as the heatproof and thermal insulation material.

Fiberglass laminates are used as the filler glass fabrics. Their mechanical properties make it possible to manufacture large-size parts. Fiberglass laminates on the basis of non-saturated polyester resins also do not require high pressure during the pressing and are used for manufacturing the large-size parts.

Material **CBAM** is the glass-fiber anisotropic material, in which glass filaments immediately on the output from the draw plates are cemented between themselves in the form of glass veneer and then they are packed as in the plywood. Bonding agents can be different. CBAM, as the structural material, has high rigidity and high impact toughness. The basic properties of thermoplastic plastics are given in Table 1.2.

Checking-up questions

1. Definition of thermosetting and thermoplastic materials.
2. Definition of polymerization (curing) process.
3. Typical representatives of thermosetting polymers.
4. Typical representatives of thermoplastic polymers.
5. Application of thermosetting polymers.
6. Application of thermoplastic polymers
7. Classification of plastics with fillers.
8. What polymers can withstand temperature more than 200°C.
9. What are main methods of plastic processing?
10. Compare specific cost of typical plastics and metals (see appendix A).

Table 1.2. Physical-mechanical properties of the thermosetting plastic

Plastics	Density, kg/м³	Ultimate temperature of long-term operation, °C	Ultimate strength, MPa			Elongation at rupture, %	Module of elasticity, GPa
			In tension	In tension	In tension		
Powder plastics	1400	100…110	30	50…150	60	0.3…0.7	6.3…8
Fiber-filled molding material	1350...1450	110	30...60	80...150	50...80	1...3	8.5
Asbestos fiber plastic	1950	200	40…50	110	70	4...3	18
Fiberglass material	1700...1900	280	80...500	130	120...250	1...3	20
Getinax	1300...1400	150	80...100	160...290	80...100	1...3	10
Textolite	1400	125	65...100	120...150	120...160	1...3	5...10
Asbestos-textolite	1600	190	55	120	140	1...3	20
Wood laminate plastics (ДСП)	1350	140...200	180...300	100...180	140...280	2...3	18...30
Fiberglass laminate	1600...1900	200...300	250...600	210...260	150...420	1...3	18.9...30
CBAM	1800...2000	200	350...1000	350...450	500...700	1...3	25

Theme 2. RUBBER

Rubber is called the product of special treatment (vulcanization) of the mixture of natural rubber and sulfur with different additives.

Rubber possesses the high elastic properties, which are inherent in natural rubber (NR) (caoutchouc) - the main initial component of rubber. It is capable of the very large strains (tensile strain reaches 1000 %), which are almost completely reversed. At normal temperature rubber is in highly elastic state, and its elastic properties are retained over a wide range of temperatures.

The modulus of elasticity lies within limits of 1…10 MPa, i.e. it is less than for other materials.

The special feature of rubber is its low compressibility (for the engineering calculations rubber is considered incompressible). Poisson ratio is equal to 0.4…0.5. The relaxation nature of strain is another special feature of rubber. During the operation of thick-walled parts (tires) as a result of the low thermal conductivity of rubber an increase in the temperature decreases its fitness for work.

Besides the noted special features high resistance to the abrasion, gas- and water-tightness, chemical stability, insulating properties and low density are characteristic for the rubber materials.

Structure and the classification of rubber

The natural or synthetic rubber, which determines the basic properties of rubber material, is the basis of any rubber. Different additives (ingredients) are infused for an improvement in the physical-mechanical properties of natural rubbers. Thus, rubber consists of natural rubber and ingredients, examined below.

1. **Curing substances** - they form the three-dimensional grid structure of vulcanized rubber. Sulfur, selenium, and peroxide for some natural rubbers commonly are used. Accelerators of curing process: polysulfides, oxides of lead, magnesium - influence the conditions of vulcanization and the physical-mechanical properties of curing agents. Accelerators develop the greatest activity in the presence of the oxides of some metals (for example, zinc), therefore called in the composition of rubber compound as activators.

2. **Antiagers** (**antioxidants**) retard the aging process of rubber, which leads to deterioration in its performance properties. There are antioxidants of chemical and physical action. The antioxidants of chemical action delay the oxidation of natural rubber as a result of their NR rubber. Physical antioxidants (paraffin, wax) form surface protective films, they are used more rarely.

3. **Plasticizers** facilitate the processing rubber compound, increase the elastic properties of NR, increase the frost resistance of rubber. Paraffin, vase-

line, stearic acid, bitumens, dibutyl phthalate, vegetable oils are introduced to NR as plasticizers.

4. According to the effect on the natural rubber **fillers** are subdivided into: active (amplifying) and inactive (inert). **Active fillers** (carbonic carbon black, powdered silica gel, the oxide of zinc) increase the mechanical properties of rubber: strength (up to 10 times), resistance to abrasion, hardness. **Inactive fillers** (chalk, talc, and barite) are introduced for the reduction of prices of the cost of rubber.

Frequently into the composition of rubber compound is introduced **regenerate** - the converted product of old rubber articles and by-products of rubber processing industry. Besides a reduction in the cost the regenerate increases the quality of rubber, decreasing its tendency toward the aging.

5. **Pigments** mineral or organic are infused for coloring rubber. Some coloring substances (white, yellow, green) absorb the short-wave part of solar spectrum and by this they shield rubber from the light aging.

The properties of natural rubbers are similar to the properties of thermoplastic polymers. The process of the chemical interaction of natural rubber with the sulfur in the technology is called vulcanization.

Depending on a quantity of introduced sulfur different frequency of the grid of polymer is obtained. Wide-spaced grid is formed during the introduction to 1…5 % of **S,** and rubber is highly elastic, soft. With an increase in the content of sulfur reticular structure more frequent, rubber becomes more solid, and upon maximally possible (approximately 30 %) saturation of natural rubber by sulfur, the solid material, called ebonite, is formed.

The molecular structure of polymer and its physicomechanical properties is changed during the vulcanization: tensile strength and elasticity of natural rubber grows, and plasticity almost completely disappears (for example, natural rubber has an ultimate tensile strength σ_B= 1.0…1.5 MPa, after the vulcanization σ_B= 35 MPa); hardness and wear resistance increase. Many natural rubbers are soluble in the solvents; rubber only will swell in them and are more stable to the chemicals. Rubbers have higher thermal stability. Natural rubber is softened at a temperature of 90℃, synthetic rubber works at a temperature more than 100°C.

The consumption of natural rubber composes approximately 30 % of entire world consumption. It is known more than 250 forms of synthetic rubber.

According to the designation rubbers are subdivided into **rubber of general purpose** and **special-purpose rubber**.

Rubber of the general purpose

Natural rubber (caoutchouc, from words "cao" – tree, "utchu" – to cry) is the polymer of isoprene (($C_5H_8)_n$). It is dissolved in the gasoline, the benzene, the chloroform, carbon disulfide, etc., forming the viscous solutions, used as the glues. During the heating above 80-100°C the natural rubber becomes

plastic and at a temperature of 200°C it begins to decompose. At a temperature of -70°C natural rubber becomes brittle. Usual ly natural rubber is amorphous. For obtaining rubber natural caoutchouc is vulcanized by sulfur. Rubbers on basis of the caoutchouc differ by high elasticity, strength, by water- and gas- impermeability, by high electrical insulating properties.

Depending on the percentage of styrene it is released several marks of the natural rubber: СКС-10, СКС-30. СКС-50. The more fraction of styrene the higher the strength of rubber, but the lower its frost resistance.

According to the structure, the chemical and physical-mechanical properties synthetic isoprene rubber is close to the natural rubber. Industry manufactures natural rubbers СКИ-3 and СКИ-3П, intended for obtaining electrical insulating rubber, СКИ-3В - for the vacuum engineering.

Rubber of the general purpose can work in the medium of water, air; dilute solutions of acids and alkalis. The interval of operating temperatures is from -35 to 130°C. From these rubber tires, belts, pipes, conveyor belts, insulation of cables, different mechanical rubber goods are manufactured.

Special-purpose rubber

Special rubbers subdivide into several forms: oil and gasoline resistant, heat-resistant, light-ozone-resistant, wear-resistant, electrotechnical, stable to hydraulic fluids. Oil and gasoline resistant rubber are obtained on the basis of the natural rubbers: chloroprene (Nairit), butadiene acrylonitrile rubber and polysulfide rubber (Thiokol).

Here are some examples of the marks of the natural rubbers of this group: СКН-18, СКН-26, and СКН-40. Rubbers on this basis are used for the production of belts, of conveyor belts, pipes, the oil and gasoline resistant rubber.

Heat-resistant rubbers are obtained on the basis of natural rubber СКТ - synthetic heat-resistant rubber. The natural rubber of mark СКТВ is resistant to the heat aging (operating temperature from -55 to 300°C).

Introduction into the main chain of the polymer of the atoms of boron, phosphorus increases the thermal stability of rubbers to 350…400°C and their gluing ability. Silicone rubbers short-term withstand temperature to 3000°C.

Cold-resistant rubbers of grades СКCS-10, СКД have operating temperature to -60°C.

Light-ozone-resistant rubbers are produced on the basis of those containing fluorine (СКФ), ethylene-propylene (СКЭП), butyl rubber.

Rubbers on the basis of fluorine-containing elastomers and ethylene-propylene are used for the sealing articles, the diaphragms, the flexible hoses, etc. They do not fail during the work under the atmospheric conditions for several years.

Butyl rubber possesses resistance to oxygen, ozone and other chemical reagents. It is intended for the work in the contact with the concentrated acids

and other chemicals; furthermore, it is used in the tire production (period of the service of tire-covers 2 times higher than these from the natural rubber).

Wear-resistant rubbers are obtained on the basis of the polyurethane natural rubbers СКУ. Rubbers on basis of the СКУ are used for the automobile tires, conveyor belts, armatures of pipes and grooves for the transportation of abrasives, foot-wear, etc.

Electro-technical rubbers include the electrical insulating and electrical conductive rubber. Electrical insulating rubber, used for insulation of the current-conducting core of wires and cables, for the special gloves and the foot-wear, are manufactured only on the basis of non-polar natural rubbers and butyl rubber.

Electrical conductive rubbers for the shielded cables are obtained from the natural rubbers НК, СКН, the Nairit.

Rubber, stable to the effect of hydraulic fluids, is utilized for sealing of the movable and stationary joints of hydraulic systems, pipes, diaphragms, pumps; for the work in oil is used rubber on the basis of СКН, whose swelling in the liquid does not exceed al- properties of rubber they are given in Table 2.1.

The influence of the factors of operation on the properties of rubber

In the process of operation rubber articles undergo different forms of aging (light, ozone, thermal, radiation, vacuum, etc.), which decreases their fitness for work; a change in the properties can be irreversible. A change in the properties is evaluated according to a change in the strength and bending characteristics and according to the restorability of rubber (change of the amount of strain in the time after the removal of load), or resistance to tear (stress concentration). The strength of natural rubbers, even without the fillers, is 20…30 MPa. The service life of rubber with the dynamic load is determined by fatigue strength.

Under the action of atmospheric conditions, ozone the cracking of stressed rubber occurs. Light causes the photooxidation of natural rubbers. The speed of aging rubber in the stressed state is higher than in the free state. An increase in the ozone resistance is achieved by the introduction of the corresponding ingredients and by the deposition of protective film (from polyurethane). The periods of service or storage of articles made of rubber are determined by a change in the residual compressive strain, which for the sealing materials is allowed to 80 %.

For forecasting the storage time of the properties of rubber it is used the combined method, which unites the running tests of polymeric material with those accelerated. The following relationship is used:

Table 2.1. Physical-mechanical properties of rubbers and carbon rubbers

Group by function	Type of rubber	Density of rubber, kg/m^3	Ultimate strength, MPa	Tensile strain, %	Residual elongation, %	Temperature, °C	
						operational	of brittle-ness
General purpose	НК	910...920	24...34	600...800	25...40	80...130	-40...-62
	СКВ	900...920	13...16	500...600	10...45	80...150	-42...-68
	СКС	919...944	19...32	500...800	12...20	80...130	-48...-77
	СКИ	910...920	31.5	600...800	28	130	-58
Special purpose:							
Oil-benzene-resistant	Nairit	1225	20...26.5	450...550	10...20	100...130	-34
	СКН	943...986	22...33	450...700	15...30	100...177	-48
	Tiokol	1300...1400	3.2...4.2	250...550	20...40	60...130	-40
Chemically proof	Butyl rub-ber	920	16...24	650...800	30...45	up to 130	-30…-70
Heat-resistant	СКТ	1700...2000	35...80	360	4	250...325	-30...-74
Heat-chemical proof	СКФ	1800...1900	7...20	200...400	2…10	250...325	-40
Wear-proof	СКУ	1900	21...60	350...550	2...28	130	-21...-50

$$\left(t_1/T_1\right)+\left(t_2/T_2\right)=1\,,$$

where t_1 – time, during which article operates (or stored); it composes small part of T_1 – complete period of the service of article; t_2 - time of reaching/achievement of the specific values of the selected indices during the accelerated aging; T2 – time of reaching of the limiting values of the same indices for the articles, which were being subjected the accelerated aging.

Thermal resistance. The strength of chemical bonds in the macromolecules and their structure determine the thermal resistance of polymers. at elevated temperatures (above 150 ℃) organic rubbers lose stren gth after 1…10 hrs of heating, rubber on the basis of heat-resistant natural rubbers can at this temperature work for a long time. At a temperature in hundred and thousands of degrees the thermal resistance is determined by the loss of half of the mass of polymer in 30 min (for example, for the natural rubber HK this temperature is 330℃).

Action of minus temperatures. Highly elastic properties decrease at low temperatures and even completely may be lost; transition into the glassy state and the increase of the rigidity of rubber occurs.

The effect of the ionizing emission on rubber is called radiation aging. Nature of rubber, ingredients, shielding additives (antirads), medium of the operation of natural rubber have an influence on the resistance to radiation. Urethane rubbers are most stable to the aging.

Rubber on the basis of CKH and HK are widely used in nuclear engineering for manufacturing the sealing rubber technology parts.

Action of vacuum. Rubber sealers can work in the vacuum at different temperatures, in the aggressive media, under the high pressure. Drawbacks in rubber are gas permeability, generation of gas, thermo-oxidizability.

According to vacuum stability rubbers are divided into:

- stable in the vacuum (thermal-vacuum durability higher than thermo-oxidizing) - СКИ-3, СКД, СКМС-10, СКЭП, СКФ-26, СКТФ-50, СКТФ-100;
- stable in the vacuum (thermal-vacuum durability lower than thermo-oxidizing) - СКТ, СКТВ-1 СКТФТ-803;
- unstable in the vacuum - СКУ, ПХП, СКН-40, СКФ-32.

Checking-up questions

1. Definition of structural rubber.
2. Classification of rubber by application.
3. Main components of rubber.
4. Mechanical properties of rubber products.
5. Characteristics of general application rubber.
6. Characteristics of special application rubber.

7. Influence of sun radiation, temperature, oxygen medium and vacuum on rubber products properties.

8. Application of rubber in aerospace engineering.

9. The notion of rubber ageing.

10. Typical process of rubber products manufacturing.

Theme 3. INORGANIC GLASSES

Glass is the name of amorphous substance obtained by supercooling of liquid melts. As a result of gradual increase of viscosity glasses get mechanical properties of rigid bodies. The process of glass-transition should be reversible.

The inorganic glasses are received by supercooling of liquid melts of inorganic compounds and their mixtures, which represent high-viscous melts. During glass-transition from liquid melted state into hard amorphous state under fast cooling the viscosity of a melt is growing and its irregular structure remains unchangeable. In this connection the inorganic glasses are characterized by disorder and inhomogeneity of their internal structure.

There should be at least one glass-forming oxide in any inorganic glass. The glass-forming oxides of silicon, boron, phosphorus, germanium, arsenium, generating a structural grid and modifying oxides of natrium, potassium, lithium, calcium, magnesium, barium, varying physicochemical properties of glass mass, are in the structure of inorganic glasses. Besides, there are oxides of aluminum, iron, lead, titanium, beryllium etc., in glass structure. Those compounds do not form a structural framing independently, but can partially substitute glass-forming oxides and thus add necessary characteristics to glass. That's why the industrial glasses are composite multi-component systems.

Glasses can be classified by a number of features: by glass-forming substance, by content of modifiers and by required utilization.

Glasses, under chemical nature of glass-forming substance, are subdivided on silicate (SiO_2), alumina-containing (Al_2O_3–SiO_2), borosilicate (B_2O_3–SiO_2), alumina-borosilicate (Al_2O_3–B_2O_3–SiO_2), alumina-phosphate (Al_2O_3–P_2O_5) etc.

Under content of modifiers - alkaline and alkali-earth metals – glasses are subdivided into:

- Alkali-free, in which the content of the indicated oxides is less than 2 % (for example, quartz glass, E-glass etc.);

- Alkaline without heavy oxides or with their low content (sodium; potash and potash-sodium glasses);

- Alkaline with the high content of heavy oxides (for example, silicate-lead and barium glass).

Under required utilization all glasses are subdivided on technical (optical, illuminating engineering, electrotechnical, chemical-laboratory, instrumental, tube), structure (window, shop-window, reinforced, glass blocks) and everyday (empties, glassware, mirrors etc).

General properties of glass

When heating is applied, the glass is melting during a temperature interval, which depends on a structure. For industrial silicate glasses the temperature of a glass transition is t_c = 425…600° C, the temperature of softening t_p is within the limits of 600…800° C. Within temperature range t_c, and t_p glasses are in high-viscous plastic condition. All manufacturing processes of glass wares mass production are carried out at the temperature higher then t_p (1000…1100° C). The properties of a glass, as well as all amorphous bodies, are isotropic.

The mechanical properties of a glass are characterized by a high compressive strength (500…2000 MPa), low structural limit at tension (30…90 MPa) and bending (50…150 MPa). A modulus of elasticity is high (45…100 MPa), Poisson's ratio is μ = 0.184…0.26. The glass hardness, as well as other inorganic materials, is frequently determined by an approximate method of scratching by Moos' mineralogical scale and is equal 5…7 units (10 units are accepted for the diamond hardness, 1 unit – for the talcum hardness). The glass is fragile; its impact elasticity is low (1.5…2.5 кW·s/m^2). Alkali-free and quartz glasses have higher mechanical characteristics. The optical properties are the main specific properties of glasses. Translucency, reflection, dissipation, absorption and refraction of light are among them. The usual not colored sheet glass transmits up to 90 %, reflects approximately 8 % and absorbs about 1 % of visible and partially infrared light; The ultra-violet radiation is absorbed almost completely. The quartz glass is transparent for a ultra-violet radiation. The factor of refraction of glasses is 1.47…1.96, the dissipation factor (dispersion) is in the range between 20…71. The glass with the large content of **PbO** absorbs X-radiation.

The glass thermal stability characterizes its life at different temperature changes. It is determined by a temperature difference the glass can maintain without destruction during abrupt cooling in water (t=0 °C). The glass thermal stability can be evaluated by the M.Bartenev's formula

$$\Delta T = K \frac{\sigma_{bend}(1-\mu)}{\alpha E},$$

where ΔT – a temperature difference, °C; K – a factor (at cooling of the whole article K = 1); σ_{bend} – structural limit under bending; μ – Poisson's constant; α – a temperature coefficient of a linear dilatation; E – a modulus of elasticity.

For the majority of kinds of glasses the thermal stability oscillates from 90 up to 170° C, and for a quartz glass it is 800…1000° C. The chemical resistance of glasses depends upon their composition.

Rapid cooling strengthening and thermal hardening can raise the glass

mechanical strength and thermal stability.

The rapid cooling strengthening consists of glass heating to temperature above t_c with consequent fast and uniform cooling in airflow or in oil. Thus the static load resistance increases in 3…6 times, toughness in 5…7 times. The glass thermal stability also increases during rapid cooling strengthening.

Thermal chemical hardening is based on deep modifying of glass structure and its surface properties. The glass undergoes strengthening in heated silicone organic liquids. As a result a polymeric film forms on a surface of a material. The rising of strength and thermal stability can be obtained by etching of a strained glass by hydrofluoric acid. As a result the surface defects, lowering its quality, are removed.

Silicate triplex glass represents two sheets of a strained glass (thickness – 2…3 mm), pasted together by a transparent elastic polymeric film. Non-sharp debris, which are formed under the process of triplex glass destruction, are held on a polymeric film. Triplex glass can be flat or bent.

Thermopan is a triplex glass consisting of two glasses and air spacing between them. This air interlayer provides a thermal insulation.

Application of technical glasses

Triplex glass, thermopan and strained glasses are mainly used for a glazing of vehicles.

The optical glasses used in optical instruments and instruments, are subdivided into crown glass distinguished by small refraction, and flint glass distinguished by large values of refraction factor. Heavy flint glasses do not transmit x-ray and radiation. Light-diffusing glass contains fluorine in the structure.

Due to high thermal and the chemical resistances quartz glass is applied to laboratory ware manufacturing. Silica glass is close to quartz glass in its properties. But it is more practically feasible and is used for electrobiunique bulbs, forms for a precise casting etc. Electrical-conducting (semiconducting) glasses, such as chalcogenide and vanadium oxide are widely used as thermistors and photoresistors.

Out of all classes of glasses silicate glasses, consisting mainly of silicon dioxide SiO_2, are most widely used in electronic engineering.

Among the main advantages of silicate glasses are their high enough electro-physical characteristics, heat-resistance, chemical resistance, hardness, transparency, low density (2000…2500 kg/m^3), cheapness and availability, simplicity of industrial production technology.

The forming of glass articles can be realized by blowing (electro-vacuum-tube bottles, etc), extraction through filament extrusion device, immersed into glass mass (sheet glass, tubes etc.), pressing, roll stock and casting. Method of continuous glass fiber drawing is of great importance. It is used for optical waveguides manufacturing and also for woven fiberglasses and fiber-glass-reinforced plastics. The glass article annealing is made to prevent appearance or to remove available residual stresses arising at cooling. Then the articles

are cooled under given mode.

The main imperfection of silicate glasses is their high brittleness, connected with the presence of microscopic defects (cracks, gaps, actuations, disturbance of density and structure of a material etc.), caused by different factors (crystallization, features of technique of obtaining and processing of articles). The mechanical strength of glasses depends more upon thermal and chemical processing of articles, rather than upon glass chemical structure. Therefore different methods of strengthening of a given chemical glass structure are used in engineering. Those methods can be jointed in two groups:

The first group – the processing techniques of a glass article surface, which modify (change) structure of their surface or simply remove defective surface layer.

The second group – the methods of regulation of internal glass structure by creation of glass-ceramic materials (vitrocrystalline material, pyroceram) and simulated orientation of structure of an amorphous or crystalline material during obtaining of filaments (for example, filaments from a quartz glass) or "whiskers" (for example, whiskers of crystal). Their strength exceeds the strength of original materials in several times (for example, quartz glass and crystal).

Heat insulation-sound proofing fiberglass materials

These materials have loose-fiber structure with large number of air interlayers and irregular layout of fibers in them. Such structure adds to these materials small volumetric weight (20…130 kg/м^3), low heat conduction [λ= 0.030…0.049 W/(m·K)].

The sorts of fiberglass materials are the glass wool (its application is limited by its brittleness): glass mats, consisting from fiberglasses located between two layers of a glass fabric or glass net, quilted by glass filament. They are applied in temperature range from -60 up to 600° C. Sometimes fiber glasses combine with a thermosetting resin adding more steady friable structure to mats. They work at the temperature of up to 150 °C. The materials, manufactured from a short fiber and synthetic resins, are known as plates. The acoustic absorption coefficient of plates at frequency 200…800 Hz is 0.5 and at frequency of 8000 Hz – 0.65.

Glass wool, mats, glass plates are applied usually to heat insulation and sound proofing of cabins of airplanes, bodies of motor vehicles, railway trams, diesel and electric locomotives, hulls, in refrigerating engineering and for insulation of different pipe lines, autoclaves, etc.

Checking-up questions

1. Definition of inorganic glass.
2. Typical composition of inorganic glasses.
3. Classification of inorganic glasses by chemical composition and appli-

cation.

4. How to determine thermal stability of inorganic glass.
5. General properties of inorganic glasses.
6. Application of inorganic glass in aeronautical structures.
7. What is the average hardness of glass by mineralogical scale?
8. Typical process of inorganic glass products manufacturing.

Theme 4. GLASS-CERAMIC MATERIALS

Glass-ceramic materials (vitrocrystalline, pyroceramics) can be received by the method of glasses directed crystallization at injection catalysts of crystallization in the melted glass. There is a growth of crystals of the basic phase (silicates) on these directed centers of crystallization. Glass-ceramic materials occupy intermediate position between inorganic glasses and ceramics. Glass-ceramic materials differ from glasses with polycrystalline structure, and from ceramics - with more thin and homogeneous microcrystalline structure.

According to their structure glass-ceramic materials are amorphous-crystalline substances. Therefore it is possible to consider glass-ceramic materials as the composite materials consisting of numerous crystals in the size up to 1 micron and having residual glassy phase. In manufacturing of glass-ceramic materials, ceramics and composite materials, the main principle of modern material science is realized - the creation in volume of constructional material the given complex of properties, heterogeneous, discrete structures. The content of a crystal phase in glass-ceramic materials achieves approximately 95 %.

Due to fine-grained crystal structure glass-ceramic materials have good enough physic-mechanical properties: high mechanical durability (approximately in 10 times is stronger than a rolling glass), high hardness and stability to attrition, high temperature of a softening (up to 1350°C) and thermal-stability (300…700°C), small density (2300…2800 kg/m^3), low factor of temperature expansion, good insulating properties, and also very small or zero water absorption.

Glass-ceramic materials can be received by the directed crystallization of silicate, borate and other glasses. Crystallization will be carried out so that growth of crystals occurred on big enough number of the crystallization centers in regular intervals distributed on all glass volume.

At present it is known more than 1000 compositions of different glass-ceramic materials both on the silicate and on another basis. Today the glass-ceramic materials technology allows using of all methods of formation of products from a glass (pressing, hire, exhaustion, blowing etc.). This makes it possible to realize their major advantages: obtaining practically nonporous articles and the manufacture of the articles of intricate geometric shape and large dimensions, which distinguish technology of glass from technology of ceramics.

The glasses with structures capable to overcooling up to a solid condition practically without crystallization can be used for reception of glass-ceramic materials, for example: **$Li_2O–Al_2O_3–SiO_2$**, **$MgO–Al_2O_3–SiO_2$**, **$CaO–Al_2O_3–SiO_2$** etc.

Glass-ceramic materials can be classified according to the different criteria. Depending on the kind of initial raw material they can be subdivided on technical glass-ceramics and slag glass-ceramics (for the first time they were

received in the former USSR on the basis of waste products of ferrous and nonferrous metallurgy - blast-furnace slags, thermal power stations ash, etc.). Depending on the method of manufacture **photocerams** and **thermocerams** can be differed.

Photosensitive glass-ceramics are obtained by short-wave electromagnetic irradiation of annealed glass products. These glasses contain, as catalysts ions of photosensitive metals therefore there is a photochemical process of restoration of ions Ag^+, Cu^+, Au^+, promoting to crystal nucleus formation. After irradiation the product is subjected to heat treatment under the special conditions. As a result of crystallization the product is strengthened. If not all surface of a product is irradiated but certain sites, only the irradiated volumes of a glass crystallize during thermal treatment. As crystallized sites of products are much more easily dissolved in acids than volumes with glassy structure, it allows to receive with the help of etching in products (substrates and others) apertures, hollows etc. Usually ultra-violet radiation is used for irradiation. As the photosensitive ordinary alkali-silicate glasses proved to be suitable. Abroad photosensitive glass-ceramics is named as photocerams.

Thermocerams are received from glasses of systems **MgO–Al$_2$O$_3$–SiO$_2$**, **CaO–Al$_2$O$_3$–SiO$_2$** and others, by addition of well-milled crystallization catalysts (**TiO$_2$**, **FeS**, **ZnO$_2$**, **F** etc.) dissolving during glass melting, into charge makeup. In this case the crystallization occurs as a result only of one heat two-stage processing, without the preliminary irradiation. The obtained glass mass is used for products forming. The cooled product again is heated up under the specific conditions – it is subjected to heat processing in one or several stages. At first only the origin of crystals is observed, and already then - their growth. At the first stage at a temperature T=500…700°C, i.e. lower, than temperature of a softening, the crystal nucleus of fluorides, sulfides or other substances are formed and grow. These nucleus create a frame strengthening a product and opposing to its deformation at the further rise of temperature. At the second stage temperature is increasing up to value T=900…1100°C and products are withstood in order to crystallize the basic substance of a glass - various silicates. According to crystal structure thermo-cerams remind porcelain.

Slag glass-ceramic is received on the basis of blast-furnace slags and catalysts (sulfates, powders of iron etc.); compounds of fluorine are entered for intensification of crystallization.

In contrast to the ordinary glass, which properties are defined basically by its chemical mixture, the structure and phase composition for materials are of key importance. The reason of valuable properties consists in their exclusive fineness, almost ideal polycrystalline structure. Glass-ceramics properties are isotropic. There is no porosity in them completely. The shrinkage of material at processing is negligible. The high abrasive resistance makes them insensitive to superficial defects.

Properties of glass-ceramic materials

The density of glass-ceramic materials lies within the limits of 2400…2950 kg/m^3, bending strength σ_{ben}= 70…560 MPa, σ_b= 110…160 MPa, σ_c= 700…2000 MPa, the module of elasticity 84…141 GPa. Durability of glass-ceramics depends on the temperature: the strength of material is decreased insignificantly up to the temperature 700…780°C; it falls rapidly at higher temperatures. Thermal stability of glass-ceramics under loading is in limits of 800…1200 °C. The maximal temperature of a softening t_{soft}= 1250…1350 °C. Impact of toughness glass-ceramics is higher, than glass impact toughness; however they are related to fragile materials. Their hardness approaches hardness of the hardened steel (microhardness 7000…10500 MPa). They are rather wear-resistant. The coefficient of temperature expansion lays in limits of (7…100)·10^{-7} 1/deg. On the thermal conductivity glass-ceramics as a result of the increased density exceed glasses. They have high thermal stability – 500…900 °C. Glass-ceramic materials have high chemical stability to acids and alkalis, are not oxidized even at high temperatures. They are gastight and have zero water absorption. They are good electric insulators.

Application of glass-ceramic materials

Application of glass-ceramic materials is determined by their properties. They are especially advisable under the conditions of deterioration, acting on abrasives and aggressive media. Because of the low friction factor at work in pair with metals, possibility to work without greasing and having high wear resistance, glass-ceramics are used in manufacturing of sleeve bearings working at temperature up to 550…580°C without greasing. Glass-ceramic materials are used for details of internal combustion engines, pipes in the chemical industry, covering of vacuum electronic devices and details of radio electronics. Glass-ceramic is used also as heat resisting covering for protection of metals against action of high temperatures. They are applied in manufacturing of textile machines, grinding abrasives, synthetic fibers drawing nozzles. Glass-ceramic materials can be used for blades of air compressors and nozzles of jet engines, for manufacturing of precision calibres and for bases of metal-cutting machine tools.

In electronic engineering adjusting, condenser and vacuum glass-ceramic materials are utilized. Wide interest was caused by lithium-silica-alumina glass-ceramic. It turned out, that it's possible to receive optically transparent materials with zero or even negative factor of temperature expansion. Glass-ceramic materials are used for manufacturing of substrates of thin-film hybrid integrated circuits, substrates for attenuators in microwave-devices, support for charge eliminators fastening.

Glass-ceramic materials, which have the factor of thermal expansion, a lit-

tle exceeding factor of thermal expansion of steel are used for manufacturing of enamels. They moisten steel well in the fused condition. After the formation of the fine-grained structure in a layer of enamel the compressive stresses because of difference in values of thermal expansion factors of enamel and steel appear; therefore protective layers of enamel is not cracked.

Due to transparency, resistance to thermal impacts (from -70 up to 700^0 C) and with factor of thermal expansion close to zero, glass-ceramics are used for manufacturing the astromirrors of telescopes. The requirement to a surface of a telescope is to keep constant curvature irrespective of an ambient temperature. These materials also used for windows of various astrophysical devices and in atomic engineering for manufacturing of reactor control rods. The lack of boron-containing steel control rods is that boron absorbing thermal neutrons can be entered into steel only in limited quantities. Therefore boron-containing rods are heavy.

Checking-up questions

1. Definition of glass-ceramic materials.
2. Typical composition of glass-ceramic materials.
3. Classification of glass-ceramic materials.
4. General properties of glass-ceramic materials.
5. Application of glass-ceramic materials in aeronautical structures and other branches of national economy.

Theme 5. CERAMIC MATERIALS

Ceramics is the name of the inorganic polycrystalline materials received by special processing of mineral compositions with the subsequent firing (sintering) of a formed and dried semi-finished item.

The term ceramics derives from the Greek word "κεραμωσ", which means "clay". Earlier the term "ceramic" was used for identification of only inorganic materials made on the basis of clay. Now not only clay-containing materials refer to ceramic, but also other inorganic polycrystalline materials. They are produced on similar technology, in which basic operation is the high-temperature burning (firing). Those materials have similar phase structure. Technical, building and art ceramics can be distinguished.

The concept of technical ceramics includes the big group of artificial ceramic materials of various chemical and phase structures created under certain heat treatment conditions. The phase structure differs in each particular case by some properties.

The important advantage of technical ceramics is opportunity of reception of products with a complex of preset properties by variation of ceramic mass structure and manufacturing technology. At present ceramic materials are applied widely in modern electronic engineering.

Ceramic constructional materials have such properties, as heat-resistance, waterproofness, resistance to active chemical reagents, incombustibility, and absence of residual strains. They do not age under the prolonged influence of electrical and thermal loads.

Technology of ceramics manufacturing

The technology of ceramic materials manufacturing consists in the preparation of initial components by sorting, crushing, milling and separations, their careful mixing and reception of a mix of initial components. The semi-manufactured article, having the form of a product, is carried out by pressure molding or pressing (cold, hot, hydrostatic etc.), by pulling through a contactor tube of the certain form, by suspension moulding, rolling or by sintering of inorganic substances. Mechanical processing, decoration, metallization and other kinds of surface processing of finished articles can be applied if it necessary.

As the method of powder metallurgy, the ceramic technology is practically wasteless, and therefore it is widely used. The special feature of ceramic products technology consists in the imparting to the product necessary operational properties at a completing stage of their manufacturing - during sintering of mixture. The separate components of this mix frequently haven't necessary properties. Oxide ceramics is applied widely as a constructional material in engineering.

For manufacturing the insulating of housing of lamps, panels of the elec-

trical inputs and other parts the ceramics of high fire resistance is used. Products from high fire resistance ceramics can be received from pure refractory metals and their compounds - oxides, carbides, borides, silicides etc. The received products have high thermal stability and chemical resistance.

The ceramic material represents the complex system generally consisting of three phases: crystal, amorphous (glassy) and gas (as a rule, in the form of non-intercommunicating cells).

The crystal phase represents the certain chemical compounds or solid solutions. This phase makes a basis of ceramics and determines the values of mechanical durability, thermostability and its other basic properties.

Glassy phase exists in ceramics as the layers of a glass connecting a crystal phase. Usually the ceramics contains 1…10 % of glassy phase, which decreases mechanical durability and worsens thermal parameters. However, the glass-forming components (clay substances) facilitate manufacturing techniques of products.

The gas phase represents the gases located in the ceramics voids. According to the state of this phase ceramics can be subdivided on dense, without open voids and porous. Presence of even closed voids is undesirable, because mechanical durability of material is reduced.

The majority of kinds of special technical ceramics have the dense sintered polycrystalline structure.

Ceramics on the basis of pure oxides. Basically the following oxides may be used in the production of oxide ceramics: Al_2O_3 (corundum), ZrO_2, MgO, CaO, BeO, ThO_2, UO_2. Such ceramics have single-phase polycrystalline structure. The melting temperature of pure oxides exceeds 2000°C; therefore they can be defined as high-refractory material. Oxide ceramics has high durability at compression in comparison with durability at tension or bending. There is significant internal pressure on the border between crystals, that's why fine-grained structures are more durable.

With an increase in temperature durability of ceramics is reduced. Oxidizability is the important property for using the materials in the range of high temperatures. The ceramics from pure oxides, as a rule, is not subject to oxidation.

The ceramics on the basis of Al_2O_3 (alumina ceramics, corundum) has high durability, which is retained at high temperatures, and chemical stability. It is excellent electric insulator. Thermal stability of corundum is low. Products from it are applied widely in many areas of engineering, for example: cutting tools for high speeds of cutting, calibers, draw plate for the drawing of steel wire, details of high-temperature furnaces, bearings, details of pumps, spark plugs in engines of internal combustion. Ceramics with dense structure are used as vacuum ceramics, porous ceramics - as heat-insulating material.

The ceramics on the basis of magnesium and calcium oxides are resistant to action of the basic slags of various metals, including alkaline. Their

thermal stability is low.

The ceramics on the basis of beryllium oxide differs with high heat conductivity that add to it high thermal stability. The strength characteristics of this material are low. Beryllium oxide has the ability to dissipate ionizing radiation, has high factor of thermal neutrons delay. It is applied to manufacturing of firepots, for melting of some pure metals and as vacuum ceramics in nuclear reactors.

The ceramics on the basis of thorium and uranium oxides has high melting temperature, but has high density and is radioactive. These kinds of ceramics are used in manufacturing of firepots for melting of rhodium, platinum, iridium and other metals, in the designs of electric furnaces, for the fuel elements in power reactors.

Example problem 5.1.

Circular specimen made MgO ceramics is subjected to 3-point bending test (ASTM Standard C 1161, "Standard Test Method for Flexural Strength of Advanced Ceramics at Ambient Temperature"). Calculate minimal required radius of the specimen (without fracture) if flexural strength σ_{fs} is 100 MPa, applied lateral load is 450 N and spacing between supports is 50 mm (Fig. 5.1).
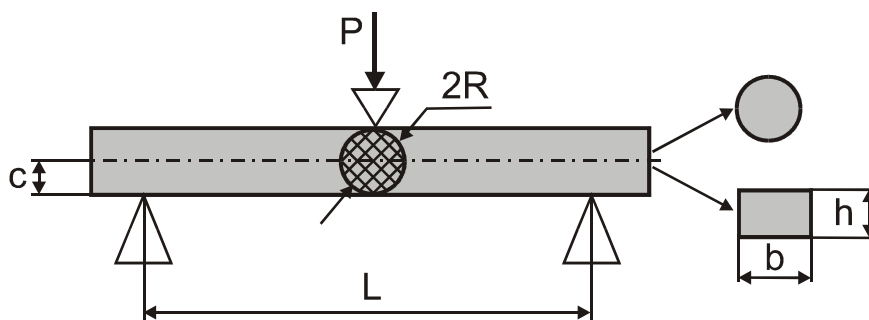

Fig. 5.1. Scheme of three-point bending test of ceramic specimens

Flexural stress of circular or rectangular beam can be estimated by known formulas from Mechanics of Materials course – $\sigma_{bend} = M/(cI)$, where M is bending moment, c is distance for neutral axis to outer fibers of a material, I is inertia moment of specimen cross-section. Then

$$\sigma_{fs} = \frac{3PL}{2bh^2} \text{ (rectangular) and } \sigma_{fs} = \frac{PL}{\pi R^3} \text{ (circular)}.$$

Using the second formula one can find that minimal R is 4.2 mm.

Example problem 5.2.

Cracks presence in ceramics leads to not only to brittle material behavior but also reduces sharply tensile strength of ceramics due to significant stress concentration at the tip of a micro-crack. This theory was developed by Griffith and value of maximum stress σ_{max} appeared at tip of crack with radius r can be estimated as

$\sigma_{max} \approx 2\sigma\sqrt{a/r}$, where σ is uniform stress at specimen edge, **a** is crack distance form the side (Fig. 5.2). Using this approach compute maximum tensile stress σ which can be applied to Sialon ceramics having ultimate strength at tension 60 ksi.

The length of the crack **a** is 0.01 inch and radius of the tip is 100 $\overset{\circ}{A}$ (39.4·10⁻⁸ inches).
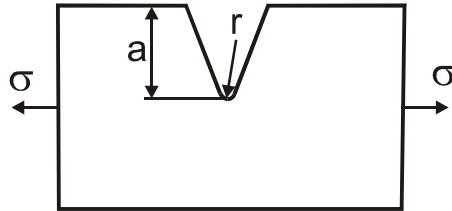

Fig. 5.2. Demonstration of ceramics crack sensitivity to cracks

If maximum stress is more than ultimate tensile strength a crack will propagate, therefore 60,000 psi $\approx 2\sigma\sqrt{0.01/(39.4\cdot10^{-8})}$, then σ=189 psi.

The basic properties of ceramics on the basis of pure oxides are given in Table 5.1.

Oxygen-free ceramics. The compounds of elements with carbon (**MeC** – carbides, **Me** – is metal), with boron (**MeB** – borides), with nitrogen (**MeN** – nitrides), with silicon (**MeSi** – silicides) and with sulfur (**MeS** – sulfides) are refered to refractory oxygen-free compounds. These compounds have high fire resistance (2500…3500°C), hardness (sometimes as diamond hardness) and wear resistance with respect to the aggressive media. Materials possess high brittleness. Carbides and borides resistance to oxidation at high temperatures is approximately 900…1000°C; it is a little lower then in nitrides.

Carbides. Silicon carbide **SiC** (silicized carbon, carborundum) has received wide application. It has high heat resistance (1500…1600°C), high hardness, stability to acids and instability to alkalis; it is used as heating rods, as graphite protective covering and as abrasive.

Borides. These compounds have metal properties; their electrical conduction is very high. They are wear-resistant, are hard and stable to oxidation. Diborides of refractory metals (**TiB₂, ZrB₂)** are widely spread in engineering. They are alloyed with silicon or dicilicides, which makes them persistent up to melting temperature.

Nitrides. Nonmetallic nitrides are high-thermostable materials having low heat conductivity and electrical conductivity. They are insulators at usual temperature and semiconductors - at high temperatures. With an increase in the temperature the factor of linear expansion and thermal capacity are increased. Hardness and durability of these nitrides is less, than hardness and durability of carbides and borides. They are resistant to oxidation and action of fused

Table 5.1. Properties of ceramics on the basis of pure oxides

Oxide	Melting temperature, °C	Density (theoretical), kg / m3	Strength, MPa			The module of elasticity, GPa	Hardness on Moose	Linear expansion coefficient, $\times 10^{-6}$, 1/deg	Coefficient of heat conductivity, W/(m·K)	Resistance to heatstroke	Resistance to erosion
			At tension	At bending	At compression						
Al_2O_3	2050	3990	260	150	3000	382	9	8.4	36.2…6.08 (100…1600 °C)	High	High
ZrO_2	2700	5600	150	230	2100	172	7…8	7.7	1.95…2.44 (100…1400 °C)	Low	High
BeO	2580	3020	100	130	800	310	9	10.6	218.6…151.1 (100…1600 °C)	High	Average
MgO	2800	3580	100	110	1400	214	5…6	15.6	34.4…6.57 (100…1600 °C)	Low	Average
CaO	2570	3350	110	80	1800	180	4…5	13.8	13.8…8.37 (100…400 °C)	Low	Average
ThO_2	3050	9690	100	100	1500	140	7	10.2	10.4…3.34 (100…1000 °C)	Low	High
UO_2	2760	10 960	130	150	980	164.5	6	10.5	9.8…3.4 (100…1000 °C)	–	–
1. Average oxidation resistance. 2. The temperature of test is specified in brackets.											

metals.

Nitride of boron is the typical representative of oxygen-free ceramics. It is soft white powder proof to neutral and regenerative atmosphere. It is used as a fire-resistant lubricant, and products from it are heat-resistant. The sintered nitride of boron is good insulator at 1800°C in the oxygen-free environment. The purest nitride of boron is applied as a material for streamlined covers of aerials and other electronic equipment of flying devices. Diamond-like nitride of boron with the cubic structure, called El'bor, is another modification. Its density is 3450 kg/m^3 and melting point 3000 °C. It is the substitute of diamond, resistant to oxidation up to 2000 °C (diamond begins to be oxidized at a temperature 800°C).

Nitride of silicon is more stable in air and in the oxidizing atmosphere up to 1600 °C than other nitrides. At high temperatures nitride of silicon exceeds all constructional materials in strength-to-weight ratio, while on cost it is cheaper in several times than heat resisting alloys. It is applied in engines of internal combustion (the head of the block of cylinders, pistons etc.). It is resistant to corrosion and erosion and it does not fear superheating the thermally loaded details.

Silicides differ from carbides and borides with semi-conductor properties and oxidation resistance; they are stable to action of acids and alkalis. They can be used at temperature of 1300…1700 °C. For example, sintered **MoSi$_2$** is used for gas turbines blades, nozzle inserts of engines; it is used as a firm lubricant for bearings, for coating of refractory metals from high-temperature oxidation.

Sulfides. Only molybdenum disulfide (MoS$_2$) with its high antifrictional properties has found practical application. It is used as dry vacuum-stable lubricant. Its operating temperatures are: on air from -150 to 435 °C, in vacuum to 1100 °C, in the inert environment to 1540 °C. Molybdenum disulfide is electricity-conductive, non-magnetic, and resistant to the radiation, the water, inert oils and acids. Properties of oxygen-free ceramics are given in Table 5.2.

Checking-up questions

1. Definition of ceramic materials.
2. Typical composition of ceramic materials.
3. Classification of ceramic materials.
4. Typical technologies of ceramic articles manufacturing.
5. General properties of ceramic materials.
6. Application of glass-ceramic materials in aeronautical structures and other branches of national economy.
7. What is the main difference between structural ceramic and sitalls

properties?

8. Conduct comparison of polymeric, metal and ceramic matrices application for structural composites.

9. Determine flexural strength of rectangular ceramic specimen (width is 2.5 inches, thickness is 1 inch) subjected to 3-point bending test at normal atmospheric conditions. Applied load is 650 N and spacing between supports is 40 mm (see Fig. 5.12).

10. What is the linear expansion coefficient of typical structural ceramics.

Table 5.2. Properties of oxygen-free ceramics

Type of ceramics	Melting temperature, °C	Density, kg/m³	Strength at 20° C, MPa			The module of elasticity, GPa	Linear expansion coefficient, ×10⁻⁶, 1/deg	Coefficient of heat conductivity, W/(м·K)
			At tension	At bending	At compression			
Silicon carbide **SiC**	2600	3200	155	190	2250	394	5.2	16.7 (200…1400)
Titan diboride **TiB₂**	2980	4520	140	246	1350	250	8.1	26
Boride nitride **BN**	2350	2340	50…110 (25); 0.7…1 (1000)	50… 110	500…600	8.65 (25); 1.16 (1000)	7.51	15…12.3 (300…1000)
Silicon nitride **S₃N₄**	1780… 1820	3200	80	160	1500	317	2.75	30
Molybdenum disicilide **MoSi₂**	2030	6240	28 (980)	473 (980)	1130 (20); 340 (1400)	430	S. 3	48.5 (900)
The note: In brackets the operational temperature (in °C) is specified.								

Theme 6. COMPOSITE MATERIALS

Application of structural materials with the increased physicochemical, technological and performance properties is one of the ways of the creation of good-quality, reliable and economic constructions in machine building. Many branches of mechanical engineering need the materials with presence of special magnetic, optical and other properties, which possess high strength, high heat resistance, high temperature strength, high cracking resistance, etc.

Traditional metals do not entirely satisfy these requirements. At the same time composite materials possess the complex of properties and special features, which make it possible to descend the mass of design with a simultaneous increase in its tactical-technical and operating characteristics. Sometimes the composite materials are generally irreplaceable.

Composite materials (CM) are the hetero-phase combinations of chemically different components with the well-defined interface between the phases. Composite materials haven't properties inherent not in one of the components individually. Usually CM consists of filler (reinforcing elements) and bonding agent (matrix).

Filler of CM has fibrous, filament, twisted, wire, strip, grid or cloth structure. Moreover structure and physical-mechanical characteristics of the reinforcing elements are considered known.

The matrix (sometimes it is called bonding agent) of CM ensures its solidity and joint operation of filaments and filler.

The filler, impregnated with bonding agent, is called **prepreg**.

The main characteristic of the creation of constructions from CM consists in the simultaneous creation of material, the development of the technological manufacturing process and planning of construction itself.

In CM high-strength filaments absorb the basic efforts, which appear in the construction under the effect of external loads, and ensure rigidity and strength in the direction of the orientation of filaments.

The reinforcing filaments must satisfy the operational and technological requirements: they must to have the required strength, rigidity, density, stability in the specific temperature interval, chemical stability, and also technological effectiveness of the production of filaments. The reinforcing components are utilized in the form of monofilaments, filaments, wires, tows, grids, fabrics, tapes. Properties of CM in this case depend not only on the properties of filaments and matrix, but also on the method of reinforcement. Structure of CM is determined by the number of layers, by their thickness and mutual orientation of unidirectional layer.

The form of the reinforcing elements is determined by method of the filaments production and by technology of the composite articles manufacturing.

Classification of composite materials

According to the type of fittings composites can be divided into those precipitation-hardened and fibrous (Fig. 6.1). The precipitation-hardened composites are the materials, in matrix of which fine-dispersed particles are evenly distributed. In these materials the matrix absorbs basic load. Precipitation-hardened composites are isotropic, i.e., have identical properties in all directions. The content of dispersed phase usually achieves 5 %.

During the creation of fibrous composites as the fittings high-strength glass, carbon, boron, organic filaments, metallic wires, filamentary crystals of the number of carbides, oxides, nitrides and other compounds are utilized.

The reinforcing materials are utilized in the form of monofilaments, fibers, wires, tows, rovings, grids, fabrics, tapes, laminas.

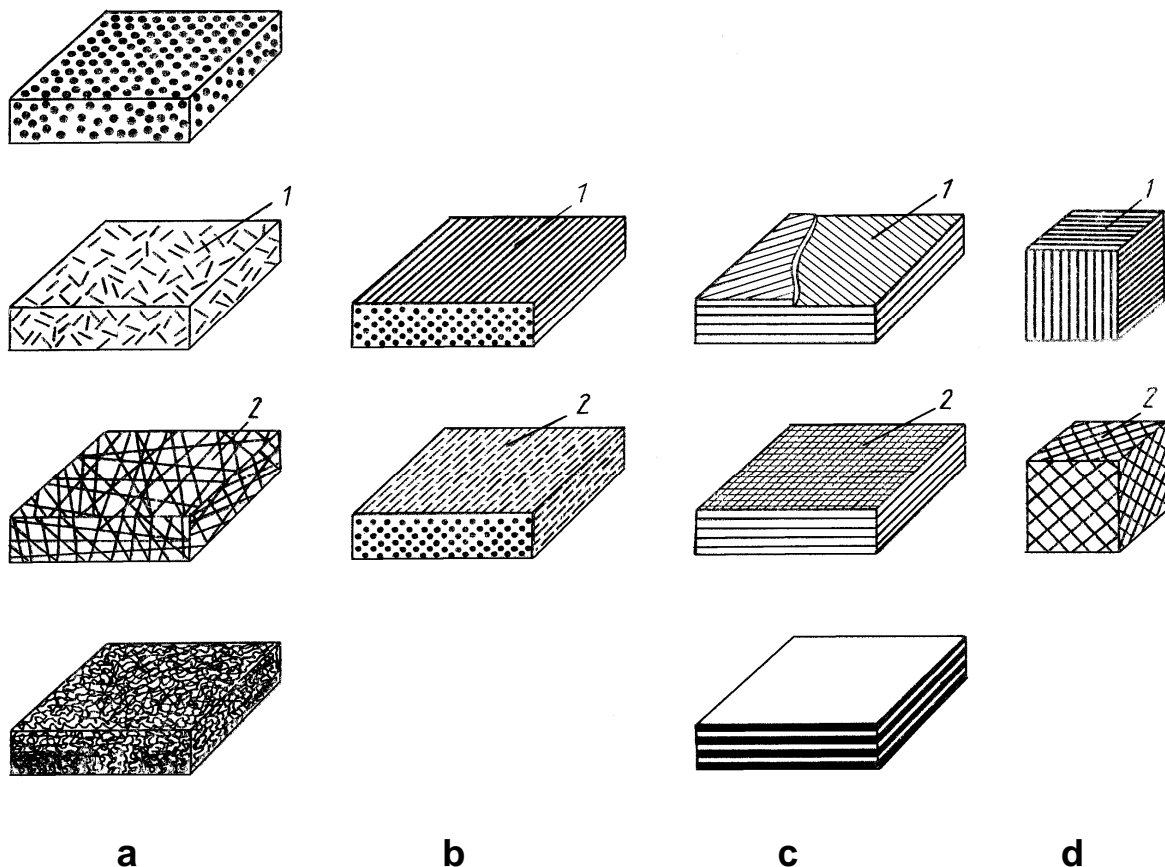a   b   c   d

Fig. 6.1. Classification of composites according to the structural criterion: **a** – chaotically reinforced (1 – short filaments, 2 – continuous filaments); b – one-dimensional reinforced (1 – unidirectional continuous, 2 – unidirectional short); **c** - two-dimensionally reinforced (1 – continuous filaments; 2 – fabric); d – three-dimensionally reinforced (1 – three families of filaments, 2 – **n** of the filaments families)

It is possible also to distinguish fibrous CM by the method of the rein-

forcement: it may be oriented or stochastic. In fibrous CM with the oriented reinforcement the fittings is furnished in the determined order, while in the stochastic - by chance. In the first case the composites possess the clearly expressed anisotropy of properties, and in the second these materials are quasi-isotropic. The ratio of the volume of filaments (filler) to the volume of entire CM is called the **volume fraction** of filler in composite. The volume fraction of filler in fibrous CM composes exceeds 55...80%.

Example problem 6.1.

Different physical, chemical, optical, electrical, thermal properties of composites can be estimated using Fick's law or the **rule of mixture**. The essence of this rule is the principle of superposition or composite final property dependence on both properties of components and their volume fraction in composite. Thus density of composite ρ_{cm} can be estimated as

$$\rho_{cm} = \sum_{i=1}^{n} \theta_i \rho_i = \theta_1 \rho_1 + \theta_2 \rho_2 + ... \theta_n \rho_n,$$

where θ_i is volume fraction of *i*-th component, ρ_i is density of *i*-th component.

Estimate density of cutting tool material made of cemented carbide (i.e. particulated composite), consisting of 75 weight % WC, 15 weight % TiC, 5 weight % TaC and 5 weight % Co. Densities of each separate components are: ρ_{WC}=15.8 g/cm^3, ρ_{TiC}=4.9 g/cm^3, ρ_{TaC}=14.5 g/cm^3, ρ_{Co}=8.9 g/cm^3.

$$\theta_{WC} = \frac{\dfrac{75}{15.8}}{\dfrac{75}{15.8} + \dfrac{15}{4.9} + \dfrac{5}{14.5} + \dfrac{5}{8.9}} = \frac{4.8}{8.7} = 0.547, \quad \theta_{TiC} = \frac{\dfrac{15}{4.9}}{8.7} = 0.349,$$

$$\theta_{TaC} = \frac{\dfrac{5}{14.5}}{8.7} = 0.040, \quad \theta_{Co} = \frac{\dfrac{5}{8.9}}{8.7} = 0.064.$$

Applying the rule of mixture one can obtain

$$\rho_{composite} = \sum_{i=1}^{n} \theta_i \rho_i = 0.547 \cdot 15.8 + 0.349 \cdot 4.9 + 0.040 \cdot 14.5 + 0.064 \cdot 8.9 = 11.5 \text{ g/cm}^3.$$

By analogous way density of fibrous composite can be found.

According to the type of matrix such composites may be distinguished: polymeric (PCM), metallic (MCM), ceramic (CCM).

Among polymeric CM the composites on the basis of polymeric resins (polyester/polyether, epoxy, epoxy-phenol, etc.) and thermoplastics (polyethylene, divinyl-chloride, Capron, etc.) are distinguished. According to the manufacturing method it is possible to divide composites into the materials, obtained by layout, by winding, by pultrusion, by pressing, etc. One of the most effective methods of molding PCM is the method of the winding of the reinforcing fillers, on the basis of which the cylindrical, conical sections of flying vehicles, differ-

ent pipes, bottles, units of form close to the bodies of revolution are obtained.

According to the method of obtaining of metallic CM they are divided into the casting and deformable metal-composites.

From the point of view of the mechanics of composite it is possible to divide them into the load-carrying, the non-load-bearing and the special. The requirements of high strength and rigidity on the regulated levels of loads are presented to load-carrying CM. Non-load-bearing composite materials are utilized for different articles of everyday usage, enclosures, coatings, etc. At present the special composites find wide application, ensuring the achievement in the articles of the specific physical properties (high-temperature strength CM, heat-resistant, frictional, high-impact, heatproof, radio-transparent, etc.).

Matrix of CM ensures the solidity of material, it fixes the form of article, it contributes to the joint operation of filaments and redistributes load at rupture of the part of the filaments. The type of matrices determines also the method of structural design.

The most important advantage of composites is their possibility of designing the elements of construction with the predetermined properties, which most fully correspond to nature and working conditions. The diversity of filaments and matrix materials, and also diagrams of reinforcement, utilized during the creation of composite constructions, makes it possible to directedly regulate strength, rigidity, level of operating temperatures and other properties by matching of composition, change in the ratio of components and macrostructure of composite.

The compatibility of the materials of filament and matrix is important requirement during the creation of fibrous composites. The following conditions of the components compatibility may be considered:

1. Presence on the interface the reinforcing material - bonding agent of the durable bond, close to the strength of matrix, under the conditions, which ensure the maintaining the initial properties of components.

2. Adhesion bond on the interface must not fail under the action of thermal and shrinkage stresses, which appear as a result of a difference in the temperature coefficients of the linear expansion of filament and matrix.

3. Absence of the chemical interaction between the reinforcing material and the bonding agent.

The properties of composites depend not only on the properties of filaments and matrix, but also on the methods of reinforcement. Composite can be formed from the layers, reinforced by the parallel continuous filaments (their properties are determined by the properties of unidirectional layer), reinforced by fabrics, with the chaotic and three-dimensional reinforcement. During calculations of physical-mechanical characteristics of CM, determinations of the stress-strained state of constructions the concept of the angle of monolayer orientation is used. The angle of laying is the angle between the longitudinal direction of monolayer and the prescribed coordinate system. Fibrous reinforcement makes it possible to create material and article simultaneously within

the framework of the same technological process. In this case it is necessary to note that in the general case, the sequence of laying the monolayers in the package influences its stress-strained state.

Specific lightweight composite structure is so-called "sandwich" one (Fig. 6.2). A typical sandwich panel consists of upper and lower face sheets (skins) separated from each other with light filler – honeycomb (hollow or filled with foamed material) of foam. Filler can be made of polymeric composites (glass-, carbon plastic), paper, Al or Ti tape, wood, polymers (polyethylene). Main advantages of sandwich structure are light weight and high rigidity at bending and compression due to elevated inertia moment of skins refer mid line. Sandwich structures are used as wing and control surfaces panels, floor, wall and shelf structure in aeronautics, automotive, civil and ship building.
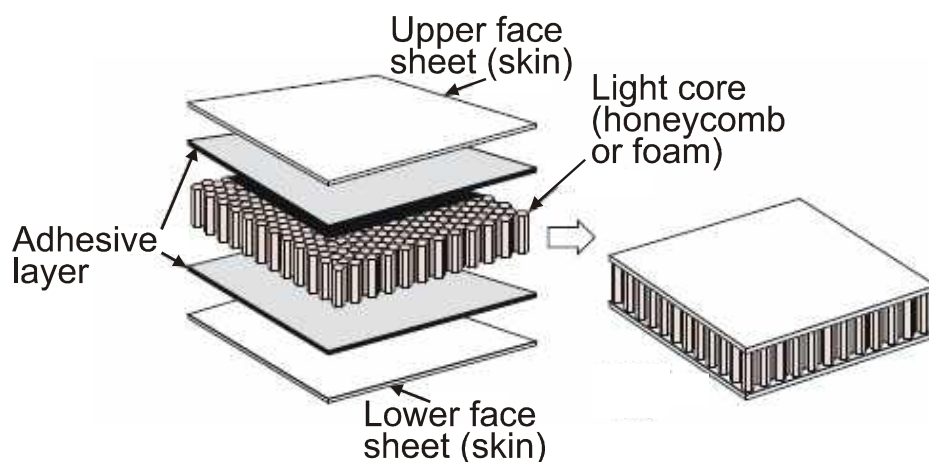

Fig. 6.2. Typical scheme of sandwich panel

Advantages and disadvantages of CM

In comparison with the existing structural materials CM possess the number of the **advantages**, among which it is possible to mark out:
- a comparatively low density;
- high specific strength and specific rigidity (carbon-fiber reinforced plastics, boron fiber-reinforced plastics and organic fiber-reinforced plastics according to the specific characteristics exceed widely used alloy Д16Т and steel ЗОХГСА);
- high chemical and corrosion resistance of polymeric CM;
- the technological effectiveness of processing CM into the articles;
- high fatigue characteristics of the fibrous CM;
- sharp reduction of a quantity of structural parts of flying vehicles units;
- special properties (radio transparency, dielectric constant, thermal conductivity, thermal diffusivity);
- capability of controlling the forces flows in the constructions due to the appropriate direction of reinforcement.

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Disadvantages of composites include:

- the high cost of majority CM in comparison with the metallic alloys;
- the anisotropy of physical-mechanical properties;
- for majority of polymeric materials - low interlayer shearing strength in the planes parallel to fittings;
- the low strength of majority polymeric CM to the bearing failure, which makes difficulties for the connections of parts by fastening elements;
- the absence of the zone of yield, brittle form of fracture, low impact toughness (Fig. 6.3);
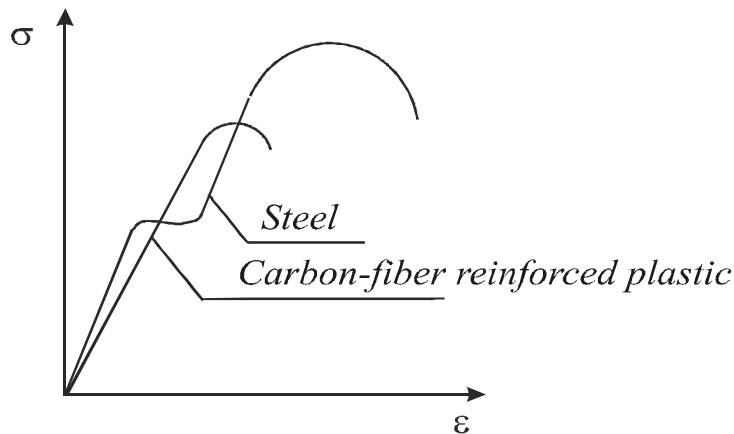

Fig. 6.3. Diagram of physical law for CM and steel

- the nonlinear nature of physical law for polymeric composites with the elongation at angle to the direction of reinforcement;
- the impossibility of shaping blanks of CM on the thermosetting matrix (by stamping, by stretch-wrap forming);
- the need of accepting the special measures for industrial safety measures during the processing of composites into the articles.

Checking-up questions

1. Definition of composite material.
2. Types of reinforcing materials used for composites.
3. Types of matrices used for composites.
4. Classification of composites.
5. Definition of reinforcing material volume fraction.
6. Typical technologies of composites manufacturing.
7. Composites advantages and disadvantages.
8. Application of composites in aeronautical structures.
9. What composites can be recommended for application at 500…600°C?
10. Main requirements to composites components compatibility.
11. What does it mean UD-composite and prepreg.

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Theme 7. REINFORCING MATERIALS FOR COMPOSITES

As the reinforcing filler in composite materials with the matrix from the synthetic resins glass, organic, carbon and boron filaments are used. Their comparative characteristic is given in Table 7.1. Furthermore, filaments on the basis of carbide of silicon, basaltic, sapphire, polyethylene filaments may be utilized. Metallic CM are reinforced by wire from steel, tungsten, beryllium, titanium, niobium and other metals. The reinforcing filaments can have a heterogeneous structure and possess the anisotropy of mechanical characteristics. Organic, aramid, carbon and boron filaments relate to the filaments with the clearly expressed anisotropy of properties. Metallic and glass fibers are considered uniform and isotropic. Let us examine the basic types of filaments.

Table 7.1. Properties of some types of fibers

The type of a fiber	Properties of fibers				
	Ultimate strength, MPa	Modulus of elasticity, GPa	Density, g/cm^3	Strength-to-weigth ratio $(м^2/s^2)\cdot10^{-6}$	Specific rigidity $(м^2/s^2)\cdot10^{-6}$
Glass fiber plastics	600	50	2.2	0.273	22.7
Carbon fiber-reinforced plastic	800	120	1.45	0.552	82.8
Organic fiber-reinforced plastic	400	40	1.2	0.333	33.3
Boron-plastic	1400	200	3.8	0.37	52.6
Filamentary crystals	30000	700	1.8…3.9	–	–
Ceramic fibers	2000…3000	400…500	3.3	–	–

Example problem 7.1

Compare specific strength and specific modulus of medium carbon steel, aluminum alloy 2024-T2 with those of glass, carbon and boron fibers. Assume that ultimate strength of Al-alloy is 500 MPa, elasticity modulus 72 GPa, density is 2.7 g/cm^3; for steel: ultimate strength is 800 MPa, elasticity modulus 200 GPa, density is 7.8 g/cm^3.

The notion of **specific strength** is ratio of a structural material ultimate (or yielding) strength to its density. The notion of **specific modulus** is ratio of a structural material elasticity modulus to its density.

Results of analysis are shown in the Table 7.2.

Table 7.2. Comparison of specific properties of typical structural materials

Materials and properties	Glass fiber	Carbon fiber	Boron fiber	Medium carbon steel	Al-alloy 2024-T2
Specific strength	0.273	0.552	0.37	0.102	0.185
Specific modulus	22.7	82.8	52.6	25.6	26.6

Glass fibers

During creation of nonmetallic structural composites – glass-fiber-reinforced plastics – glass fibers are widely used. At comparatively low density they are heat-resistant, resistant to the chemical and biological effect; have high strength and low thermal conductivity.

It is known two forms of the fiberglass: continuous and staple. For the continuous filament long length, straightness, parallel arrangement of filaments in the fiber are typical; for the staple – small length, winding and the chaotic arrangement of filaments in the space.

Most frequently the filaments, which have the form of solid round cylinder, are used. The **shaped fiberglass** include filaments with the triangle, square, hexahedron form of cross section, tapes with the smooth and corrugated surface, hollow filaments.

Technology of manufacturing. Initial technological process for production all forms of is the drawing of filaments from the molten sand mixtures.

There are three basic methods of fiberglass production: drawing of the fiber from the melt through the draw plates or spinnerets (single-stage process); drawing of the fiber from the glass beads during their heating (double-stage process); production staple fiber by the separation of the jets of glass mass under the effect of centrifugal forces or air flows, gas and vapor.

Bundle of monofilaments (in quantity of thousands) gathered into the single tow are called **fiber**.

Continuous tows (or UD – i.e. unidirectional) are used for the processing into the twisted complex filaments, the rovings and the woven materials. For guaranteeing further processing, the filaments are covered with the substances, called **sizers**. **Sizer** elevates adhesion of filaments to resin, prevents filaments abrasion wear, shields them from the destruction during the textile processing, and prevents the accumulation of the charges of static electricity with friction. During the direct processing of filaments into the articles the sizer can be eliminated. Direct sizer fulfills dual function - it protects filaments from the destruction and elevate the adhesion between the glass and the polymeric matrix.

Important characteristic of fibers and filaments is their linear density, i.e., the ratio of the mass of a filament (in grams) to its length (in km). Measuring unit of lin-

ear density is Tex - 1 Tex = 1 g/km. It relates to the thickness of materials.

Mechanical properties. Quartz fibers have the highest strength. Mechanical properties of fibers are stipulated by their chemical composition, the method and conditions of fibers manufacturing, fiber surface quality and physical-chemical interaction of surface defects with the environment. Fiberglass has the low resistance to cyclic bending and abrasion, which is considerably increased after their impregnation with varnishes and resins. Quartz, silicate, kaolin, alkali-free aluminum-borosilicate filaments possess high chemical stability to water and the high pressure vapor.

Application. Fiberglass of various composition widely is utilized as the reinforcing elements of composites in the form of the monofilaments of different diameter, filaments and tows of different thickness, tapes, fabrics of diverse braiding, mats and other non-woven materials. This is caused by the properties of fiberglass, by accessibility and abundance of raw material, also, by relatively simple technology of their production and processing.

Organic fibers

Creation of synthetic organic filaments is based on the application of high rigidity and strength of polymers. Since the density of polymeric fibers two or three times lower than density of mineral ones, specific values of their strength and rigidity in many instances are higher. An essential deficiency in the polymeric organic filaments consists in the sharp decrease of strength with an increase in the temperature, and also in low temperatures of vitrification and destruction.

Technology of production. The majority of synthetic organic fibers are manufactured by spinning from melt or solution of the polymer, with which the filaments are formed by the extrusion of viscous-flow state polymer through the fine holes in spinneret with the subsequent solidification of the emerging liquid jets. The shaped filaments then are subjected to the heat treatment, in which the particles monofilaments are sintered.

High-strength fibers are subjected to the additional thermo-drawing, in process of which occurs an increase in the modulus of elasticity by 15... 20 %.

An overall drawback of the aramid fibers is sorption of moisture, which leads to worsening in their properties approximately up to 15...20 %. Aramid fibers are characterized by a good capability for textile processing. There is technology of production the very light (with a density of 0.97 g/cm^3) fibers from polyethylene.

Properties. Fibers retain the above-indicated initial characteristics to the temperature 180℃, and with an increase in the tempera ture, without melting, it is carbonized. Cryogenic temperatures do not cause the embrittlement of fibers. Comparing with glass fibers organic ones have strength at compression especially.

Mostly aromatic polyamides are used for manufacturing high-modulus and high-strength organic fibers for aerospace application. They possess high tensile

strength and module of elasticity, thermal stability, which makes it possible to operate them in the wide temperature interval, by good shielding durability with the shock, by incombustibility, by the increased fatigue and dielectric properties.

As a result of the low density aramid filaments exceed on the specific strength all known at present reinforcing filaments and metallic alloys, being inferior on the specific modulus of elasticity to carbon and boron filaments.

Application. Organic filaments are treated into the fibers, the complex fibers, the fabrics of different weaves (linen, twill, sateen, etc.), roving, matte finishes, non-woven materials in the machines of textile and knitted production.

Organic filaments are used widely for manufacturing engine blocks of solid propellant, pressure vessels, and parts of the airframe of aircraft.

Carbon fibers

According to the mechanical and physical-chemical properties among the high-temperature fibers the carbon fibers occupy special position. According to the specific indices they exceed all high-temperature filaments. Carbon fibers have high thermal stability. Structure of carbon fibers is inherited from the source material: carbon filaments, obtained from the synthetic fibers are produced from the fibrils, they have anisotropic structure. Carbon filaments on basis of pitch and phenolic resin are isotropic and are typical amorphous carbon.

Carbon filaments are divided into the **carbonized** (temperature of heat treatment 1173…2273 K, carbon content 80…99 %) and those **graphitized** (temperature of heat treatment to 3273 K, carbon content higher than 99 %).

Technology of production. Carbon filaments are obtained only from the fibrous polymers, infusible during the heat treatment, which ensure the high output of carbon and the necessary mechanical and physical-chemical properties. Natural and chemical organic filaments serve as source material for carbon filaments production. As a result of heat treatment in the inert medium organic filaments are converted in carbon filaments.

Polyacrylonitril (PAN) and hydrated cellulose filaments are the basic forms of raw material for production carbon filaments. The promising kinds of raw material include diverse pitches, rich in carbon, and phenolic resin, from which first are obtained the organic filaments, treated then in carbon filaments.

From pitch and phenolic resin carbon filaments of average strength and with the low modulus may be obtained; however, from pitch can be obtained high-strength and high-modulus filaments. Accessibility, low cost, high carbon content (85…96 %) and high output of carbon filaments are the main advantages of pitch; deficiency – presence of cancerogenic substances in majority of them.

Mechanical properties of carbon fibers are determined by the special features of structure and depend on the presence of defects. According to the strength of carbon fibers they are divided into three groups: low-strength ($\sigma_\theta < 500$ MPa), medium strength ($\sigma_\theta = 500...1500$ MPa) and high-strength

($\sigma_в$ > 1.5 GPa). The modulus of elasticity of carbon filaments can be changed over wide limits – from 30 to 700 GPa, it grows proportional to density of carbon filaments.

Carbon fibrous materials of medium strength are produced in the form of the fabrics of different structures, yarn, filaments, tows tapes, felt, etc. The cost of carbon filaments of the medium strength considerably lower than cost of high-strength and high-modulus carbon filaments (from \$100/kg), and according to the mechanical properties they completely satisfy the requirements, presented to the materials of heatproof, thermal insulation and other designation.

Developed porosity, usually with the diameter of pores $(3...50) \cdot 10^{-4}$ µm, and very large specific surface area which reaches 2000 m^2/g during special treatment are characteristic to carbon filaments. These values can be regulated by the temperature of heat treatment, or by the type of initial filament.

The adhesion of carbon fibers to the bonding agent is increased by the removal the film of sizer from the surface of carbon filaments after the termination of textile processing. Frequently on the surface of carbon filaments is covered with filamentary crystals, which possess high shear strength (whiskering). By the value of the coefficient of thermal conductivity carbon filaments, especially graphitized close to metals. Effective thermal conductivity depends on the textile form of material. Carbon fibrous materials possess extremely high thermal stability. Carbon filaments are characterized by high chemical stability to the majority of aggressive media.

Processing. Carbon fibrous fillers are made in the form of the filaments of infinite length, bands, felt, tapes, fabrics of diverse assortment, knitted wear, etc.

Boron, carbide of silicon and Borsic fibers

Because of the high strength and rigidity, low density, the filaments of boron, carbide of silicon and Borsic (**B**/**SiC**) are prospect for the work hardening of matrices on the basis of light metals (**Al**, **Mg**, **Ti** and their alloys).

Technology of production. The filaments of boron and carbide of silicon are obtained by precipitation from the gas phase of boron and **SiC** to the heated to temperature 1370…1470 K surface of tungsten wire with a diameter of 12.5 µm. The diameter of the filaments, produced by industry is 90...150 µm. One- or two-chamber reactor, through which at a rate of 4.7…18 m/hr tungsten filament is stretched, is utilized for production the filaments. This filament is heated by electrical current. The core of boron filaments contains of borides of tungsten **WB**, **W₂B₅** and **WB₄**. During the prolonged heating phase **WB₄** retains mainly.

The ultimate strength of the fiber core is substantially lower than the ultimate strength of a whole filament.

Carbide of silicon is utilized also as a coating for increasing the heat resistance of boron filaments. This gives the possibility to introduce boron filaments into some metallic matrices, with which they actively interact, for exam-

ple, into molten aluminum. The filaments of boron, covered with the thin (3…5 µm) layer of carbide of silicon, are called the Borsic filaments. Carbide of silicon for the coating is formed according to the same reaction, according to which the continuous filaments of carbide of silicon are obtained, but in this case the base layer is not tungsten wire, but boron filament.

At elevated temperatures the strength of Borsic and silicon carbide fibers considerably overexceeds the strength of the filaments of boron. Therefore such filaments are utilized in the high-temperature materials on the basis of titanium and high-temperature alloys.

Properties. The strength of the silicon carbide fibers is decreased at a temperature higher than 1000°C. The decomposition o f boron, Borsic and silicon carbide fibers occur mainly as a result of the defects appearance on the surface of a fiber.

Application. Boron, silicon carbide and Borsic fibers are used for the reinforcement of composites as short and continuous fibers, and also in the form of the semi-finished product – preliminarily prepared unidirectional tows.

Boron fibers are susceptible to variable rigidity in comparison with other types of the reinforcing filaments. The shear modulus exceeds 180 GPa.

Boron UD-ibers are used in the production of composites with the aluminum and polymeric matrices. Composites with the aluminum matrices have a set of advantages: it is possible to use them at temperatures up to 350°C and can be machined by conventional methods.

At present boron composites are used in the production of the articles of aviation, rocket and space equipment, where the characteristic criteria of the quality of material are specific values of strength and rigidities. In general they are utilized for manufacturing of rod elements and panels, and also for strengthening of profiles and elements of airframe structures.

Metal fibers

Metal wire fibers are quite effective for application in the structural composites. Thus, for the composites, intended for the work at reduced temperatures, steel and beryllium filaments are utilized, and at temperatures more than 1500°C – tungsten and molybdenum. Mostly high-strength metal fibers are produced form corrosion-resistant steels.

For composites operating at high temperatures (1500…2000°C) tungsten filaments are most acceptable. The high-temperature strength of tungsten fibers increases due to the introduction into the tungsten and its alloys of high-melting dispersed particles (carbide, borides, silicides, nitrides.).

Precipitation from the gas phase, metallization in the vapor phase, metallization from the fusion relate to the basic technological methods of different metal coatings deposition on the fiber surface. For coating of fibers such metals as nickel, iron, moliben, zirconium, aluminum, copper, etc are used.

The optimum thickness of metal coatings must be within the limits from several micrometers to several dozens microns.

The metallized fibers are used successfully in some constructions of jet aircraft and spacecraft, for the production of filters, flexible plates, the electrodes of storage batteries, etc.

Ceramic filaments

Ceramic fibers are manufactured from strong, high-melting, chemically stable and erosion-resistant materials – oxides, carbides and borides. They are promising for the heatproof and high-temperature CM. According to the structure ceramic filaments are divided into poly- and single-crystal.

The tensile strength of polycrystalline fibers is more than the same materials in the massive form, but it is less than in the single-crystal filamentary crystals. In practice they do not differ from the massive ceramic materials by the thermal-physical and chemical properties. Average shear modulus is 170 GPa. The coefficient of temperature expansion is $3.3 \cdot 10^{-6}$ 1/deg.

Technology of production. There are three methods of the production of the polycrystalline ceramic filaments: film method, extrusion and the deformation of powder mixtures. Ceramic single-crystal fibers grow from the melts.

Application. Ceramic polycrystalline filaments are intended for the strain hardening of metals and ceramics. They are introduced into composites in the form of single continuous fibers or rods, packed in layers in the required direction. They are used also to reinforce polymeric composites for the purpose of an increase in rigidity and erosion durability. Tow or roving, which treats into the fabric, the felt, and the mats, is manufactured from the continuous filaments.

Filamentary crystals

The filamentary crystals, used for the reinforcement, conditionally are divided into the ceramic and the metallic. The filamentary crystals include also the filamentary and laminar fillers of eutectic CM. The filamentary crystals have a single-crystal structure and a diameter to 10 µm with length-diameter ratio 20... 100.

Technology of manufacturing. The filamentary crystals are produced by several methods: by cultivation from the coatings or in electric field, by precipitation from the gas phase, by chemical methods, by crystallization from the solutions, by whiskering filaments.

Properties of filamentary crystals. The determination of mechanical properties is restricted by the number of the difficulties, caused by their small dimensions. Tensile strain is approximately 3…4 %. If the thickness of filamentary crystals is more than 20...40 µm, their strength coincides with the strength of massive crystals. During the creation of structural composites the preference is given to ceramic filamentary crystals in comparison with the metallic as a result of their higher

specific characteristics, less susceptibility to softening at high temperatures and best compatibility with the metallic matrices.

Application. Filamentary crystals are used as the reinforcing fillers in the metallic, ceramic and polymeric matrices. Technology of filamentary crystals processing during the manufacture of CM consists of the following operations: the processing raw material, the application of coatings, orientation, packing, and molding.

Checking-up questions

1. Main functions of reinforcing material in composites.
2. Classification of reinforcing materials.
3. Main properties of reinforcing materials.
4. Technologies of carbon fibers manufacturing.
5. Technologies of glass fibers manufacturing.
6. Technologies of boron fibers manufacturing.
7. Technologies of organic fibers manufacturing.
8. What does it mean an active and passive sizing agent?
9. Compare specific strength of carbon-plastic, glass-plastic, boron plastic and typical metal alloys (Al, steel, Ti).
10. What does it mean 1Tex? What is the total length of tow with linear density 800 Tex in the bobbin with weight 6 kg.

Theme 8. MATRIX MATERIALS FOR COMPOSITES

Matrix is the most important component of composite. The requirements to the matrices can be subdivided into the **operational** and the **technological**. The first include the requirements, caused by the mechanical and physicochemical properties of the material of matrices, which ensure the fitness for work of composition under the effect of different operational factors. The mechanical properties of matrix must ensure the effective joint operation of reinforcing fibers in the various forms of loads. Strength characteristics of matrix material are determined with the variable loads applied to composite in arbitrary directions different from the fiber orientation, and also with the cyclic loading. Nature of matrix determines the level of operating temperatures of composite. More operation temperature less strength and rigidity of matrix materials and also adhesion between reinforcement and matrix is reduced too. Matrix also characterizes the stability of material to the effect of environment, chemical stability, thermal-physical, electrical and other properties.

Technological requirements of matrix are determined usually simultaneously by the processes of obtaining of composite and article made of it. The essence of these processes consists in the compatibility of the reinforcement matrix and the final article shape. The purpose of conducted technological operations is to guarantee uniform fibers distribution in matrix (without direct contact between themselves) with predefined fiber volume fraction, to use maximum possible fiber strength properties, to create sufficient adhesion between fibers and matrix. Therefore there are definite requirements for matrix material: good fiber wettability with liquid matrix in process of impregnation; possibility of semi-finished products manufacturing (for example, prepregs) with the subsequent articles manufacturing, high interlaminar adhesion of composite in the process of molding; low intensity of final forming parameters (for example, temperature and of pressure), small shrinkage etc.

At present composites on the polymeric, metal and ceramic matrices are most widespread.

Thermosetting and thermoplastic bonding agents (binders) are used as the matrix materials of polymeric composites.

Thermosetting binders are low-viscosity, freely soluble products (resins), capable of being solidified during the heating under the action of curing agents (hardeners), catalysts with the formation after hardening of irreversible lattice structure (low dissoluble and infusible).

Thermoplastic binders are high-molecular linear polymers (filaments, films, powders), which during the heating are melted down, and during the subsequent cooling harden and their state after hardening is reversed.

Thus, the selection of bonding agent for the composite is the complex problem, whose correct solution contributes to the creation of material with the effective technological and performance properties.

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Thermosetting polymeric matrices

Solidified thermosetting resins have the widest application as the polymeric matrix (bonding agent).

Hardening of bonding agents (binder) occurs with elevated temperatures (i.e. single component binder) or in presence of catalyst, hardener or initiator of hardening. Solvents can be added to the resin if necessary to regulate required binder viscosity.

In real composite structures phenol-formaldehyde, polyester (polyether), silicon, epoxy and polyimide bonding agents most widely are used. The properties of some bonding agents are given in Table 8.1.

The maximum operation temperature of structural composites is determined by thermal stability of bonding agent. Thermal stability is directly related to the temperature of polymer curing, since upon its reaching the modulus of elasticity is reduced sharply. At the stage of binder (matrix) selection designer has to pay attention both to the mechanical characteristics of binder and its chemical stability, dielectric properties, cost and availability.

The phenol-formaldehyde resins may be obtained by the polycondensation of phenols with aldehydes. Depending on the ratio of components and process conditions novolak or resol phenol-formaldehyde resins are formed.

The curing process of phenol-formaldehyde resins is carried out at the range of temperatures 160...200℃ under pressure of 3...4 MPa and above.

The three-dimensional polymers obtained after hardening are stable during the prolonged heating up to 200℃ and in the li mited period are capable of resisting the action even higher temperatures (several days at 200... 250℃, several hours at 250... 500℃, several minutes at 5 00...800℃). Above mentioned temperature resins begin to decompose.

The drawback of the phenol-formaldehyde resins is the large shrinkage during the hardening related to release of large quantity of volatile substances. For obtaining the material with a small porosity it is necessary to conduct high-pressure molding. Phenol-formaldehyde resins are very brittle; it is caused by the considerable residual stresses, which appear in the material during curing.

Polyester (polyether) resins are saturated esters, their mixtures between themselves or with the low-molecular monomers. These resins mainly exist in solid state, readily soluble in different solvents.

Binding agent on the basis of polyester resins can be cured both with the room, and at elevated temperatures. For the curing at both room and elevated temperature the accelerator or initiator can be used together.

Polyesters in the cured state are characterized by high resistance to the action of water, mineral oils, inorganic acids, many organic solvents, by good dielectric properties. The advantages of polyester bonding agents include low viscosity of polymers, which ensures simplicity of their joining with fibers, ability to be solidified in the wide temperature interval without the application of high pressures of

Table 8.1. Properties of typical binding agents

Resin	Binding agent					
	Ultimate strength, MPa, tension/compression	Modulus of elasticity, GPa	Density, g/cm^3	Volumetric shrinkage, %	Linear expansion coefficient $\alpha \cdot 10^5$, 1/°C	Water absorption for 24 h, %
Phenol-formaldehyde	40…70 / 100…125	7…11	1.2…1.3	15…25	6.0…8.0	0.3…0.4
Organic-silicone	25…50 / 60…100	6.8…10	1.35...1.40	15…20	2.0…4.2	0.08…0.12
Polyester	30…70 / 80…150	2.8…3.8	1.2…1.35	5…10	6.0…9.0	0.1…0.2
Epoxy	35…100 / 90…160	2.4…4.2	1.2…1.3	1…5	4.8…8.0	0.01…0.08
Polyimide	90…95 / 250…280	3.2…5	1.41…1.43	15…20	5.0…5.8	0.28…0.32

low-molecular substances, simplicity of modification by other resins.

Disadvantages of polyester resins are low level of mechanical characteristics in cured state; poor adhesion to many fillers; low compatibility of bonding agents to fibers; sufficiently large shrinkage and the presence in composition of toxic monomers (of styrene type).

Silicone resins may be obtained by the polycondensation of the products of simultaneous hydrolysis of the mixtures of chlorinesilanes. They are usually solid brittle substances.

The deposition of silicone resins on the filaments is accomplished from the alcohol solutions and more rarely - from the melt.

The hardened silicone resins differ significantly from others bonding agents by ability to operate in the wide range of temperatures (-200...+350°C), by resistance to the action of organic solvents and of mineral acids, and by high dielectric properties. Drawbacks of silicone resins include: low mechanical characteristics at room and elevated temperatures, molding articles under the considerable pressures, prolonged curing cycle.

Epoxy resins are the mixtures of oligomeric products with the epoxy groups at the ends of the links. More frequently epoxy resins of the type ЭД, ЭФ, ЭМ, ЭА are used.

Curing is accomplished in the presence of hardeners and catalysts and flows without the release of low-molecular substances and with small shrinkages. Amines and acid anhydrides are used as the hardeners. Hardener is mixed with resin or its melt. At an insufficient melting viscosity either at high melting point they are mixing with the application of a solvent, for example acetone, which then is eliminated or active diluents - low-viscosity epoxy resin (ДЭГ, ТЭГ etc.).

Advantages of epoxy resins: high mechanical and adhesive characteristics, high manufacturability of binders, long pot-life before curing. This makes it possible to make the pre-impregnated and partially hardened (near 50 %) semi-finished products (prepregs). It is possible if necessary to carry out the curing process of resins in the wide temperature range, it occurs without the release of volatile components and with a small shrinkage (1...5 %). Cured epoxy bonding agents have sufficiently high mechanical characteristics, are resistant to the action of many solvents and aggressive media, they are moisture-proof, and their temperature of operation can reach order of 150...200°C.

Disadvantages of epoxy binders are low thermal stability, which leads to the sharp loss of the strength properties at elevated temperatures, close to the temperature of the polymer curing temperature. Modified epoxy resins (with fillers) have increased thermal stability and composites on their basis can operate at temperatures up to 180...200°C.

Polyimide bonding agents. As binders these polymers can be used only at the intermediate stages of their obtaining, since at the final stage of formation they lose plasticity and solubility. These binders are applied to the fibers

from their solutions and suitable for fibers impregnation by different methods Curing of the binders occurs in the range of temperatures 300...350℃. The porosity of composites based on polyimides is 1... 3 %. Solid polyimides possess high heat- and chemical resistance, good mechanical characteristics, stability of dimensions in the wide temperature interval.

Disadvantages of bonding agents include the considerable technological difficulties of the manufacture of articles made of the materials on their basis.

Thermoplastic polymeric matrices

In recent years thermoplastic materials are used more extensively as the matrices.

Advantages of thermoplastic bonding agents are low level of the residual stresses, which relax in the thermoplastic matrix in the first hours after molding of articles, high manufacturability, possibility of recycling and articles shape correction even after curing. Technological advantages of the thermoplastics: include large range of allowable raw material and semi-finished products, the sharp reduction of the molding cycle duration due to the exception of hardeners application. Generally such wide-spread process as forming, stamping, bending, laminar combination of blanks, welding, pultrusion are used for products manufacturing. Additional prospects are opened because of reduction in the laboriousness of welding defects correction, by the action of solvents, by the local deformation of structural elements by heating, and also due to the possibility of the utilization of off-cuts and recycling of articles, which creates preconditions for the effective solution of ecological problems.

Although the level of mechanical characteristics of majority of thermoplastics at room and elevated temperatures is lower than cured thermosetting binders have, chemical stability and impermeability, as a rule, exceed them.

Fiber impregnation with thermoplastic binders can be carried out from liquid-phase or solid-phase method.

Liquid-phase method is used for manufacturing the prepregs. It consists in the deposition of bonding agents on the reinforcement (filaments, tows, tapes, films, fabrics) from the solutions or the melts. In this case the viscosity of the saturating medium is the main parameter, which determines the quality of impregnation. For the thermoplastic composites, obtained by liquid-phase method, the high porosity is typical; it exceeds in 10...15 times the porosity of composites on the basis of thermosetting bonding agents.

Solid-phase impregnation is mastered during the manufacture of the semi-finished products, in which the reinforcing filaments are combined with the thermoplastic solid state binder in the form of powder, film or filaments. The main advantage of this method in comparison with the liquid-phase impregnation consists in the penetration of matrix components into the volume of fibrous fillers before exact impregnation and the efficiency of the subsequent impreg-

nation during melting of the solid matrix inclusions is increased thus, the duration of impregnation is shortened, power consumption (pressure, temperature) are reduced, the porosity of composite is decreased.

To improve quality of impregnation with matrix powder ultrasound or by vibration effect is introduced. However, application of powders does not make it possible to obtain thermoplastic composites with the uniform degree of reinforcement throughout entire volume of composite.

Film binders permit to reduce mentioned drawback, since thermoplastic films alternates with reinforcing elements more uniformly. However, the quality of impregnation in this case depends substantially on the thickness of the reinforcing filaments, tows, tapes, and also on the complexity of the geometric form of the molded article (dual curvature, undercutting).

Matrix thermoplastic filaments are most successful with the impregnation of components in the stage of semi-finished products manufacturing. This makes it possible to create composites from prescribed by structure regularity, reliable fixation of the diagram of reinforcement at all stages of work. Articles on the basis of such filaments can be made by laying-out, winding, pultrusion, and impregnation of fibers can be conducted at the stages of weaving and braiding. The application of matrix thermoplastic filaments makes it possible to obtain the high reinforced composites with the maximum degree of reinforcement and in certain cases to create the non-matrix composites, in which the solidity of the reinforcing fibers is reached due to their welding or autohesion interaction.

Among thermoplastic bonding agents new type bonding agents, called rolivsan, occupy special position; they have the possibility to combine the high thermal stability of composite and the light manufacturability of bonding agent. Rolivsans are intended for obtaining of composites and articles with wide range of operation temperatures (270...620 K). The main advantage of rolivsans over others bonding agents is the combination of the liquid state of slightly toxic initial composition, insignificant release of incidental volatile products during its hardening with the high thermal stability and the strength of both matrix itself and composites on its basis.

Carbon matrices

The carbon matrix has similar physical-mechanical properties to carbon fibers provides high heat resistance of carbon-carbon composites and makes it possible to most fully realize in the composite the unique properties. Two methods carbon matrix obtaining are used: the carbonization of polymeric matrix of the previously molded carbon plastic blank and precipitation from the gas phase of pyro-carbon. The process of carbonization is the high-temperature working of article made of the carbon-fiber reinforced plastic to the temperature of 1073 K in the non-oxidizing medium (inert gas). The purpose of heat treatment is conversion of bonding agent into the coke. In the process of carboniza-

tion the thermal destruction of matrix occurs, which is characterized by the loss of mass, by shrinkage and by the formation of the large number of pores.

The properties of carbon matrix considerably depend on the form of initial bonding agent. As the bonding agents are mainly synthetic organic resins (phenol-formaldehyde, furan, silicon, polyimide etc.) saturated up to the high coke contents are used. For carbon matrix obtaining coal and petroleum pitch (carbon content up to 92...95 %) are also utilized. Sometimes the process of additional impregnation and carbonization is carried out, which makes it possible to regulate density and strength of material.

Properties of carbon matrices. Tensile strength is 34 MPa, during the compression – 6 MPa; the module of elasticity is approximately 50 GPa; Poisson's ratio 0.33; the coefficient of temperature expansion $3.55 \cdot 10^{-6}$ 1/deg.

Metal matrices

The metal matrices of fibrous composites are light (aluminum, magnesium, beryllium alloys) and high-temperature metals (titanium, nickel, niobium alloys).

Matrix materials on the basis of aluminum. According to the technological criterion aluminum matrices can be subdivided into several types: deformable, casting, powder. All methods of the fibers impregnation with matrix can be subdivided into the solid-phase, the liquid-phase and precipitated methods.

The solid-phase methods of fibers impregnation consists in the assembly of the packets of blanks, which consist of the alternating layers of the material of matrix and filaments, and the subsequent interconnection of the components. Liquid-phase methods are based on the use of different forms of the casting of the molten material of matrices (as a rule, this Duralumin Д1, Д6, Д16, aluminum alloy 2024, 7075, the alloys of groups АВ, АК, В95). The material of matrix ensures the impregnation (in the vacuum, at the low and high pressure) of the preliminarily packed system of fibers. The precipitation is the method of the deposition of metal layer on the fibers by the different methods (gas-phase, chemical, electrolytic) and the filling with it of interfiber space.

The most heat resistant Al-matrix based alloy is САП-alloy (sintered aluminum powder). For Al-matrix composite obtaining the method of plasma spraying of matrix material is widely used.

Titanium and magnesium matrices. As the matrix materials the magnesium alloys of MA2-1, MA5, and MA8 grades are utilized. Titanium matrices possess a good manufacturability during the hot deformation, weldability, ability to prolongedly retain high strength characteristics at high temperatures. However, these materials retain high resistance to deformation even at high temperatures, which leads to the need of utilizing regimes of superplastic deformation for obtaining of composites with the brittle filaments.

Checking-up questions

1. Main functions of matrix material in composite.
2. Classification of matrices for composites.
3. Main properties of matrices.
4. Technologies of reinforcing materials impregnation with polymeric matrices.
5. Technologies of metal and ceramic matrices joining with reinforcements.
6. What is the pot-life of ready prepreg?
7. At what temperature ranges composites with polymeric, metal and ceramic matrices can operate?
8. What alloys can be used for metal matrices?
9. What is the typical composition of ceramic matrices?
10. What are main disadvantages of polymeric matrices?
11. What polymeric matrices guarantee maximum adhesion to reinforcement?

Theme 9. BASIC PROCESSES OF COMPOSITES MANUFACTURING

Selection proper technology of composite parts and assemblies manufacturing depends on composite class, type of the reinforcement and matrix, reinforcement arrangement and other factors. As has already been mentioned above, it is possible to classify composites according to the type of the matrix: polymeric, metallic, ceramic, carbon-carbon, eutectic. Last class includes composites, in which the oriented fibrous or lamellar crystals, formed in the process of the oriented crystallization serve as the reinforcing phase.

Articles made of eutectic composites can be obtained during single operation without the application of labor-intensive processes of fibers manufacturing and their introduction into the matrix. There are precipitation-hardened and fibrous metallic composites. Precipitation-hardened composites may be obtained in two stages: first is preparation of powder mixture of reinforcing and matrix phase and then composite is molded.

Powder mixtures are obtained by the mechanical mixing of phases, by mechanical alloying, reaction and chemical mixing, decomposition of the mixture of salts, by surface or internal oxidation, hydrogen restoration in the solutions, and also by chemical precipitation from the solutions.

Molding of precipitation-hardened composites is conducted by pressing, rolling, sintering at high temperature in protective atmosphere or in the vacuum; by hot extrusion, by drawing and by rotational forging.

As a result of molding the semi-finished product in the form of monolithic ingots or thin strips is formed. Articles are obtained by machining ingot-blanks or welding the strips.

Fibrous metallic composites are obtained by spraying (precipitation) matrix to the filaments from the solutions of salts and other compounds of metals, from the steam-gas phase, from the plasma; by impregnation of filaments (tapes) with molten metal; by pressing, by rolling, by packing by the explosion of the filaments (tapes), which alternate with metal foil etc. Obtained blanks (semi-finished products) are worked into the articles made of metal composites just as in the case of the precipitation-hardened metal composites. Ceramic composites as metal composites may be precipitation-hardened and fibrous.

This class of composites is used in the constructions, operated in the conditions of very high temperatures (to 2000...3000 ℃) and the conditions of thermal shock (front edges of supersonic aircraft, nozzle for the solid-propellant engines and the uncooled combustion chambers of liquid propellant rocket engines and other parts).

Precipitation-hardened ceramic composites include ceramics, reinforced by short metal fibers. Here are examples of such ceramic (cermets): ceramics based on porcelain and tungsten fibers; ceramics based on aluminum oxide, of thorium oxide and molybdenum fibers etc.

Technology of cermets manufacturing. Components are mixed thor-

oughly in the mixer. Then they are packed in the graphite mould with the coating from boron nitride (releasing agent), then pressed at a high pressure at temperature 1250...1650℃.

Fibrous ceramic composites are impregnated with ceramic composition in porous form. Suspension of ceramic composition is pumped through the form in the vacuum. After drying, the article is subjected to hot pressing in the graphite mould under the high pressure (to 30 MPa).

Carbon-carbon composites are composites reinforced with carbon fibers and also the combined structures from the straight and woven filaments. These filaments are arranged chaotically or form the unidirectional and regulated fibrous structures, oriented in the different directions. Graphite is matrix. These materials, and ceramic CM, are used in the airplane designs, operated at very high temperatures.

Technology of carbon-carbon composites semi-finished articles obtaining is the following. Reinforcement is saturated by phenol-formaldehyde, furan, silicon, polyimide and other resins with the subsequent carbonization (transformation into the coke). The carbonization of bonding agent is conducted at temperatures of 1100... 1800℃ in the non-oxidizing medium. Precipitation to the carbon framework from the gas phase of pyro-carbon, which is formed with the thermal decomposition of hydrocarbons in the pores of fittings, is the second method of carbonization. Sometimes these technologies may be combined for obtaining the low-porosity articles.

Drawback of polymeric composites manufacturing is the high technological power consumption related to such severe curing parameters as large pressures (5...50 MPa) and temperatures (200…300℃).

For some classes of composites separate manufacturing processes (both preparatory and basic) are combined.

Preparatory manufacturing processes

The production of articles made of polymeric composites begins from the preparatory manufacturing processes, which include; the preparation of the reinforcing materials, the preparation of bonding agent, the manufacturing of reinforced semi-finished products (prepregs, premixes, tablets) and consequent cutting of semi-finished products.

The preparation of the reinforcing materials includes its inspection in as-received condition, desizing, finishing, warping.

Incoming inspection consists in testing of initial reinforcement for correspondence to the technical requirements of physical-mechanical characteristics.

Desizing is the removal of sizer from the surface of fibers (if necessary) for increasing their adhesion to at the subsequent stages of manufacturing.

Finishing is the deposition on the surface of the fibers (if necessaery) of the hydrophobic coatings, which increase the wettability of filaments with the

bonding agent.

Warping - rewinding of one either several fibers, tows, tapes or fabrics from original bobbin to another one to separate fiber from each other after storage and conduct visual observation of fiber quality.

The preparation of bonding agents. Before fibers impregnation binder has to be checked on required properties, life-time and suitability.

Bonding agent (binder) consists of exact pure polymeric resin(s) of definite composition, hardeners, catalysts, solvents, plasticizers, anti-retardants and pigments. Incoming control of binder includes checking its composition, measuring parameters of dynamic viscosity (concentration), surface tension etc.

Hardener is chemically active substance, which causes the reaction of polymerization (curing) or polycondensation and transforms binder into the solid irreversible state.

Catalyst is the substance, which accelerates the reaction of hardening (curing). Sometimes the retarders of reaction are introduced instead of the catalysts.

Plasticizer is chemically neutral substance, which imparts ductile properties to composite in the hardened state. High plasticity increases the resistance of polymeric composite to cracking with the impact loads during the operation.

Solvent is chemically neutral substance of low viscosity, which ensures a good impregnation of fittings. Solvent after impregnation is evaporized from the compound in the form of volatile products.

Preparation of prepregs. The forming of the articles made of polymeric composites is manufactured with two methods: "wet" and "dry". With the "wet" method impregnated with bonding agent reinforcement is immediately used for composite manufacturing.

With the "dry" method pre-impregnated with the bonding agent and slightly dried prepregs are used. This method makes it possible to store prepregs prolongedly in the fridge, expands the nomenclature of initial resins and therefore it is more efficient. The impregnation of prepreg includes three stages: the deposition of bonding agent on the reinforcing material, its filtration into the pores of reinforcing material and their uniform filling, and also fixing bonding agent in the prepreg via drying.

Cutting of semi-finished products is the process of manufacturing the optimum number of blanks of prepreg. Blanks must ensure the high quality of article at the stage of its laying-up (absence of folds, the minimum of overlaps). This process is selected into the separate, if the large number of blanks of the woven prepregs complex on the form is required.

Basic processes of polymeric composites manufacturing

Forming is the manufacturing process of getting article with required shape, fibers spatial arrangement, dimensions. These parameters at the stage

of forming are still being unsteady and reversible, since they are ensured only forming jig. Therefore, it makes high requirements on the jig rigidity and precision. Since "wet" or "dry" formed article stays on the same jig and on the subsequent stage of **molding**, then it makes to it the same requirements, which ensure the consumer quality of article.

It is possible to distinguish 4 basic methods of composites forming: **laying-up**, **winding**, **spraying**, **pultrusion** and combination of these methods.

The method of laying-up. Manufacturing process of laying-up (Fig. 9.1) includes:

- forming jig surface preparation;
- consequent laying-up of monolayers in accordance with stacking sequence of composite article (has to be shown in the article drawing);
- installation of embedded items according to drawing (for example, foam inserts for edge rigidity increasing).
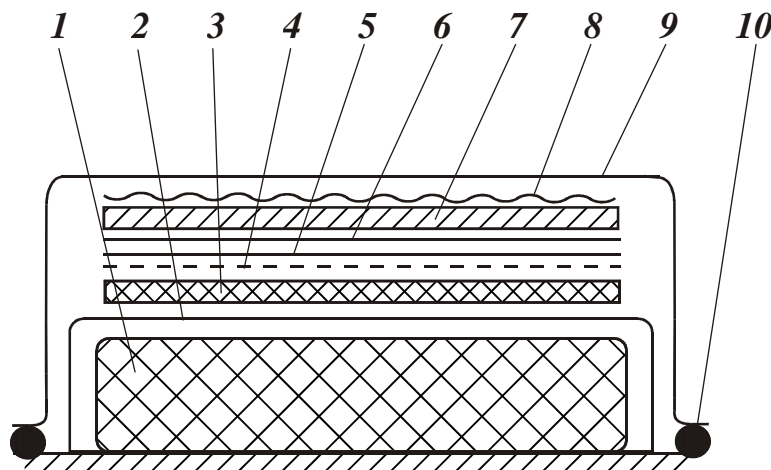
Fig. 9.1. Scheme of laying-up process: 1 – forming jig; 2 – releasing film; 3 – package of "wet" monolayers; 4 – air separating grid; 5,6 – bleeding fabric; 7 – cauling plate; 8 – protective fabric; 9 – vacuum bag; 10 – air tightening sealant

The laying-up method is used for manufacturing any parts having of plane form, single and double curvature. Laying-up is especially effective for the articles of intricate shape and having stacking sequence with a large quantity of laying elements. By the laying-up method, skin of fuselage or wing, control surfaces, load-carrying elements and other parts of aircraft are made usually.

According to the geometry of parts and possibilities of equipment laying-up processes by the method of execution may be divided into the manual, mechanized (semi-automated) and fully automated.

Manual (hand) laying-up process is used in the production of small and average-size parts of especially complex shape. Blanks are laying on the forming tool (jig). The surface of jig is preliminarily cleaned, degreased and separating layer is applied to it. Blanks are laying-up the forming surface.

Mechanized laying-up processes are used for manufacturing the parts of plane, simple or double curvature shape with the slope angle more than 5°. Package is formed on the plane table of laying-up machine or mandrel covered with separating film (see Fig. 9.1, item 2). After getting required shape the mandrel is transferred into forming equipment is rolled up by the heated (for example, rollers). The mechanized laying-up shortens manufacturing cycle, reduces laboriousness, increases the accuracy of production and eliminates clearances and overlaps.

The automated laying-up process is used during the manufacture of the parts of plane form or simple curvature with the angle of undercutting curve not more than 5° on the CNC winding machine. This metho d consists in the consecutive laying of prepreg pieces directly to forming jig.

Form and dimensions of part, presence of equipment, and volume of production limit the application of the highly efficient automated laying-up process.

Forming articles by the method of winding is accomplished for the parts of predominantly axisymmetric and close to it. However, the parts of more intricate shape (propeller blade, flaps, control surfaces) are obtained by winding too. The following schemes of winding are distinguished by the kinematics principle: turning, polishing and winding (Fig. 9.2).
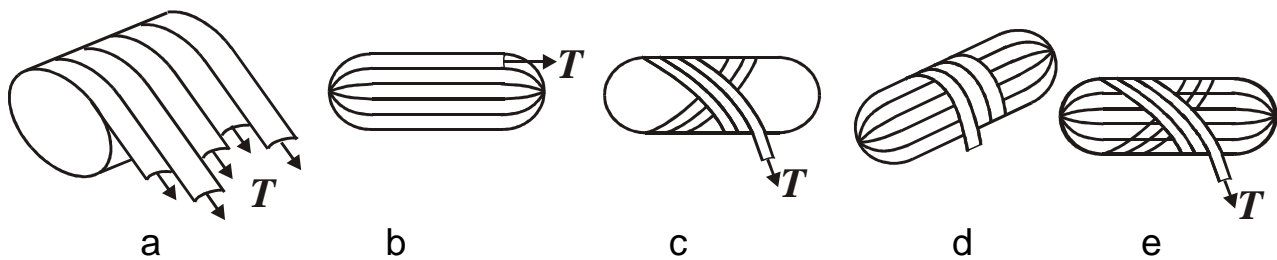

Fig. 9.2. Schemes of composite articles winding

According to the type of reinforcement (prepreg) arrangement in the wound article circular (Fig. 9.2, a), spiral (Fig. 9.2, c) and longitudinal (Fig. 9.2, b) winding are distinguished. Different combinations of these forms of winding are also utilized (Fig. 9.2, d, e).

By **circular** winding shells, housings of large diameter are formed.

Spiral winding is realized by fibers, tows, tapes and fabrics in the form of prepregs or by "wet" method. This method is used for forming housings, conical sockets of nozzles, shell of high-pressure cylinders with the bottoms, manifolds and other parts.

The **longitudinal** winding is realized with the parallel arrangement of the reinforcing elements (fibers, tows, tapes) directed mainly along article longitudinal axes. This method of winding is used for creation of large-dimension structural elements: beams, spars, rods, trusses, propeller blades. All types of winding are very effective manufacturing processes, which ensure high productivity and quality of article and coefficient of material usage. These manufactur-

ing processes are realized on the specialized winding facilities.

Forming by the method of **pultrusion** (Fig. 9.3) consists in the drawing of the impregnated reinforcing material (most frequently in the form of bundle of fibers or roving) through the forming tool (spinneret, draw plate, rollers). The advantage of this method is high technological effectiveness and productivity. The main drawback of the method is constant cross-section of an drawing article and low productivity of manufacturing (several sm/min).
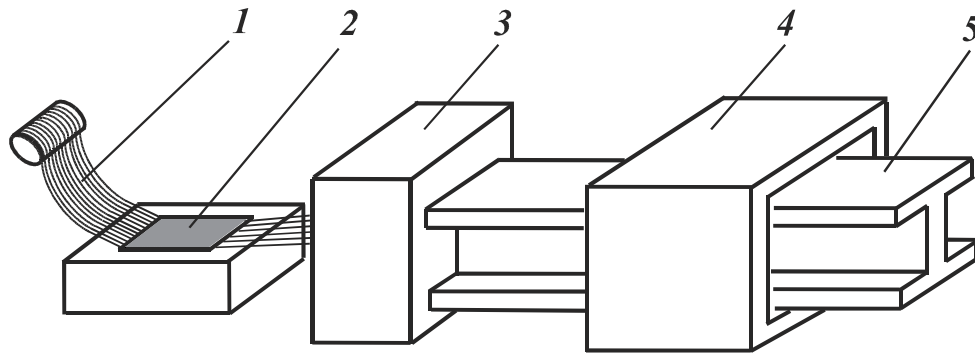
Fig. 9.3. Scheme of pultrusion process: 1 – dry fibers; 2 – bath with binder; 3 –forming tool (spinneret); 4 – drying furnace; 5 – ready article

Forming by the method of **spraying** (Fig. 9.4) consists in the deposition on the jig surface the mixture of the chopped fibers and binder. This process in the aircraft construction in practice did not find application because of the low quality of articles. It is used for manufacturing of car bodies and panels and boat hulls mainly from glass-plastics.
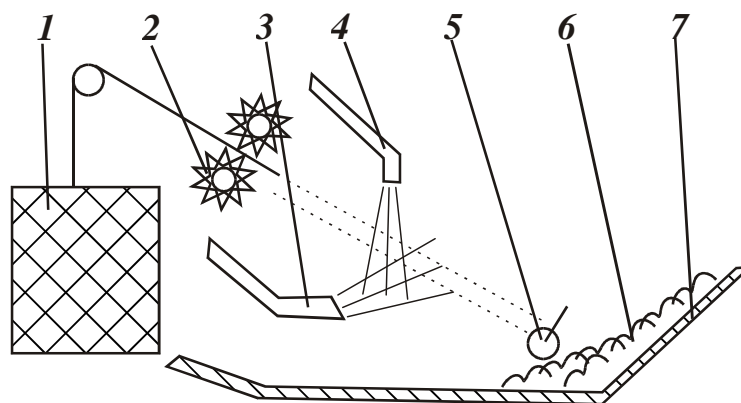

Fig. 9.4. Scheme of composite article spraying: 1 – roving; 2 – cutter; 3 – resin with accelerator; 4 – resin with catalyst; 5 – roller for compaction; 6 – wet impregnated composite; 7 – forming jig

Manufacturing processes of polymeric composites molding

Molding is the very important manufacturing processes of imparting required composite properties, final shape and dimensions to an article. There

are many methods of composite articles molding. Their selection depends on an article dimensions and shape, required level of properties (reinforcement volume fraction) type and composition of a binder and other factors.

All methods of molding can be divided into three groups: contact molding, molding in the rigid dies and elastic molding.

Each of these methods is characterized by the different values of three basic parameters: time, temperature and pressure. According to these parameters free (contact) molding, vacuum molding, autoclave (hydroclave) molding and forming may be distinguished.

Under the equal conditions (stacking sequence, type of binder and reinforcement, hardener) the strength and the rigidity of article made of polymeric composite depend on reinforcement (fiber) volume fraction.

Contact molding is used for the noncritical parts. The vacuum forming is used for the low-loaded parts. For the moderate loaded and critical parts vacuum-autoclave molding is used.

Nowadays specific variant of contact molding, so-called RTM (Resin Transfer Molding) process is widely used (Fig. 9.5). Advantage of this process is its cleanness, uniform resin distribution in originally dry reinforcement, high productivity and surface quality (due to special coating – gel-coat - application), possibility of complex shapes manufacturing. Disadvantage of this process is in necessity of individual forming jig preparation.
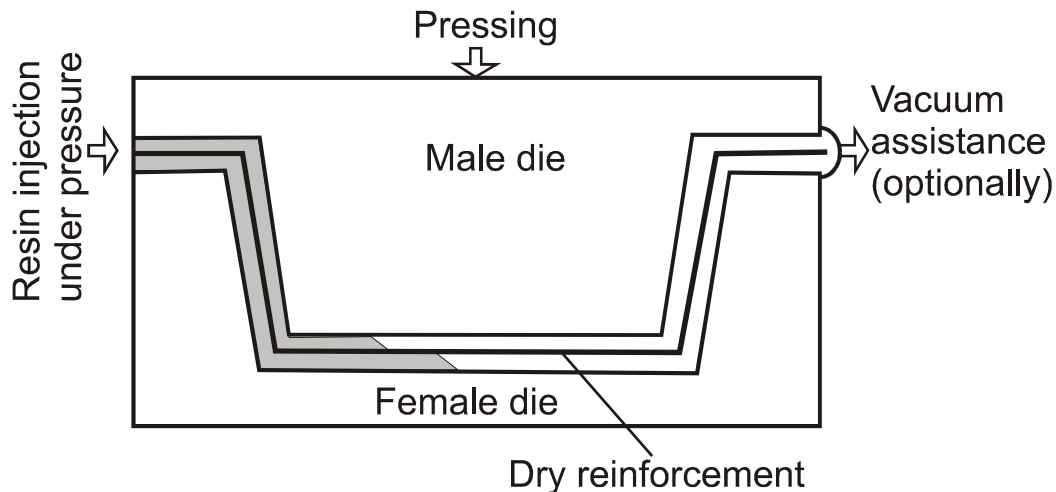

Fig. 9.5. Scheme of RTM process

Manufacturing processes of polymeric composites machining

After removing of an article from the forming tool it is machined by known engineering methods - milling, drilling, threading, cutting to make holes, cut edges, produce treads cut-outs etc.

The fundamental special features of polymeric composites machining are

presence of abrasive and viscoplastic phases (fibers and bonding agent), heterogeneity of structure and the anisotropy of properties, the possibility of burnings in the zone of cutting and other factors. The guarantee of the required quality of machining is achieved on the comparison with metal working: by a change in the geometry of cutting tool, modes of cutting (speed, feed, depth) and by the application of more strong and wear-resistant materials.

The assembling manufacturing processes depend on the form of the completing parts. It is possible to separate three basic types of the assembling: assembly from the semi-finished products (integral assembly); assembly from the semi-finished products and finished parts; assembly from the finished parts.

The first type of assembly is the process of joining several semi-finished product to a single unit on a single jig which is completed by article molding.

The second type of assembly is the process of the formation of articles made of several blanks of semi-finished product and finished articles in single unit (assembly with co-curing), that is completed by the process of molding entire unit.

The third type of assembly does not differ from conventional assembling of metal structures, with exception of the specific conditions of reciprocal fixation of elements or units. During assembling of composite articles and units are connected to each other by angle plates made of tapes. These tapes are polymerized without the heating or with the local heating in the jig of overall assembly. Adhesive joints, special joints with discrete bonding, and also metallic fastening elements (bolts, screws, rivets) are used widely, although their application requires special technological procedures.

Checking-up questions

1. Classification of manufacturing processes for composites.
2. Preparatory process of composites manufacturing.
3. Main stages of laying-up process.
4. Manufacturing of composites by winding.
5. Manufacturing of composites by pultrusion.
6. Manufacturing of composites by spraying.
7. RTM process for composites manufacturing.
8. Distinctive features of composites machining.
9. Distinctive features of composite articles assembling. Main concepts of composite units assembling.

Theme 10. METHODOLOGY OF UNIDIRECTIONAL COMPOSITE MATERIAL PROPERTIES FORECASTING

The solution of problems of structural stress-strain state determination is based on three groups of the equations: equations of equilibrium, compatibility of strains and physical law. First two groups of equations are invariant to the materials used. The physical law derived for an isotropic body has to be changed for the composites because it expresses the dependence between the stresses and the strains at the point of a solid. Anisotropic material (wood, composites) possesses different physical-mechanical properties in the different directions. Structure of the composite is characterized by the fiber volume fraction, by reinforcement orientation refer to selected coordinate system and by the sequence of layers stacking. These parameters together with the properties of fibers and binder determine physical-mechanical characteristics of complex composite generally consisting of several monolayers with different angles of laying-up: its elastic constants, strength properties, coefficients of linear thermal expansion, coefficients of shrinkage. Development methods of composite properties evaluating is based on application of different physical models of composite. The methods of UD-composite properties forecasting shown below are based on the model according to which material is considered as consequence of repeated orthotropic strips (so-called V.Vasil'yev's model).

Elastic constants of unidirectional CM

In the model of unidirectional CM reinforcing fibers are parallel to each other and located in the same plane (Fig. 10.1). The following assumptions are used during the calculation of elastic constants of composite:

1. Complete adhesion between fibers and matrix takes place.

2. Materials of fiber and matrix are isotropic and linearly elastic. In this case, physical law is written in the form (indices f and m are related to the fiber and matrix respectively):

$$E_f \cdot \varepsilon_{fx} = \sigma_x - \mu_f \cdot \sigma_y,$$
$$E_m \cdot \varepsilon_{mx} = \sigma_x - \mu_m \cdot \sigma_y,$$
$$E_f \cdot \varepsilon_{fy} = \sigma_y - \mu_f \cdot \sigma_x, \tag{10.1}$$
$$E_m \cdot \varepsilon_{my} = \sigma_y - \mu_m \cdot \sigma_x,$$
$$G_f \cdot \gamma_{fxy} = \tau_{xy}, \quad G_m \cdot \gamma_{mxy} = \tau_{xy},$$

where ε_x, ε_y – linear strain in the direction of axes X and Y respectively; γ_{xy} – relative angle strains in the plane XY respectively; σ_x, σ_y are normal stresses in composite in the direction of axes X and Y respectively; τ_{xy} – shear stresses in composite in the plane XY; E and G – elastic modulus in tension and shear respectively; μ – Poisson's ratio.
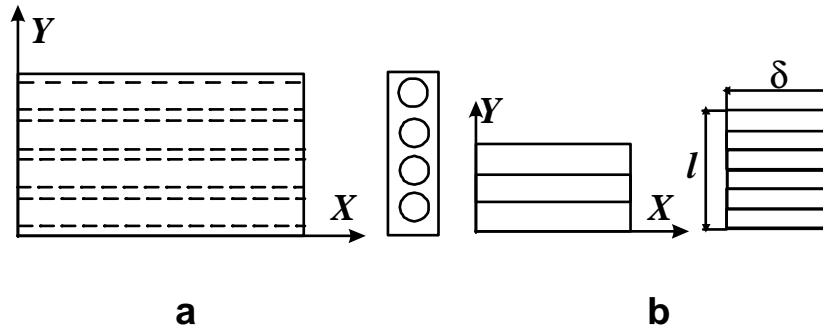
Fig. 10.1. Model of unidirectional CM: a – the diagram of real CM;
b – analytical model

3. Cross-section of composite is considered ideal (Fig. 10.1, **b**), i.e., during deformation along axis Y (across fibers) stress in fiber and matrix are the same.

Determination of elasticity modulus along fibers

Let's consider the strain occurred along axis X. Under the condition of absolute adhesion between the fibers and the matrix, the strain of fiber and matrix of composite are equal:

$$\varepsilon_x=\varepsilon_{fx}=\varepsilon_m. \tag{10.2}$$

Equilibrium equation of composite representative element at projection of forces to the axis X is written as follows:

$$\sigma_{fx}\cdot F_f+\sigma_{mx}\cdot F_m=\sigma_x\cdot F, \tag{10.3}$$

where F_f, F_m, F – are cross-sectional area of fiber, matrix and entire composite respectively. If we take into account requirement (10.2), physical law and equilibrium equation of composite element, then the elasticity modulus of composite along fibers can be determined as follows:

$$E_x=E_f\cdot\theta+E_m\cdot(1-\theta), \tag{10.4}$$

i.e., elasticity modulus of composite along the fibers is determined by the **rule of mixtures**. With the values of θ up to 0.75 relationship (10.4) gives sufficiently exact value E_x in comparison with its real value, measured experimentally.

Determination of elasticity modulus across fibers

Determination of elasticity modulus across fibers several models may be used. Some of them consider real shape of fiber, others are not. The second model gives more exact values of E_y. Let us use this model for the determination of E_y. In accordance with the assumption about the equality of transverse stress in fiber and the matrix it is possible to write:

$$\sigma_x=\sigma_{fx}=\sigma_{mx}. \tag{10.5}$$

At composite loading along the Y-axis it is deformed along the axis X also. This strain causes stresses in composite in the direction of axis X as a result of

the presence in the material of Poisson's ratio. Since external loading along axis X is absent, the composite must be in equilibrium. It is possible to determine the elasticity modulus of composite across fibers after combined solution of physical law, condition (10.5) and mentioned equilibrium conditionas follows:

$$E_y = E_f \frac{\theta(n-1)+1}{[\theta + n \cdot (1-\theta)] \cdot [\theta \cdot (n-1)+1] - \theta \cdot (1-\theta) \cdot (n \cdot \mu_m - \mu_f)^2}, \quad (10.6)$$

were $n = E_f / E_m$.

Shear modulus of UD-composite

There are several methods of composite shear modulus determination. The condition of equality of tangent stresses in fiber, matrix and entire composite leads to following solution:

$$G_{xy} = \frac{G_f \cdot G_m}{G_m \theta + G_f (1-\theta)}. \quad (10.7)$$

Coefficients of linear thermal expansion of UD-composite

Studying thermal deformation of composite is based on the assumption about isotropy of linear expansion coefficient of fiber and matrix. During heating or cooling with temperature difference ΔT composite is deformed (Fig. 10.2).
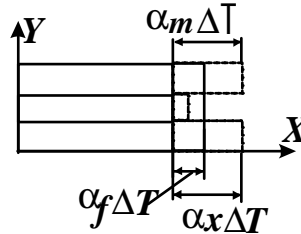

Fig. 10.2. Thermal deformation of composite

If fiber and matrix would not be jointed together, then they would obtain the free (non-restricted) strains $\alpha_f \cdot \Delta T$ and $\alpha_m \cdot \Delta T$. But combined deformation of entire composite causes strain $\alpha_x \cdot \Delta T$. Coefficients of linear thermal expansion of composite along and across the fibers α_x and α_y are equal to:

$$\alpha_x = \frac{\alpha_f \cdot E_f \cdot \theta + \alpha_m \cdot E_m \cdot (1-\theta)}{E_f \theta + E_m (1-\theta)}; \quad (10.8)$$

$$\alpha_y = [\alpha_f \cdot \theta + \alpha_m \cdot (1-\theta)] + \frac{\theta(1-\theta)(\alpha_m - \alpha_f) \cdot (E_f \cdot \mu_m - E_m \cdot \mu_f)}{E_f \theta + E_m (1-\theta)}. \quad (10.9)$$

Coefficients of UD-composite shrinkage

Polymerization of polymeric binder is accompanied by shrinkage. Real contraction of binders is from 2 to 20 % depending on the type of binder type, presence of hardener, conditions of curing etc. The result of shrinkage is decreasing of a part dimensions, appearance of residual shrinkage stresses in the components of composite. Shrinkage stresses worsen the strength properties of composite. It is necessary to note that the shrinkage coefficient of the majority of fibers ζ_f is close to zero. The shrinkage coefficients of composite along and across fibers ζ_f and ζ_m are determined as follows:

$$\varsigma_x = \varsigma_m \frac{E_m(1-\theta)}{E_f\theta + E_m(1-\theta)},$$
(10.10)

$$\varsigma_y = \varsigma_m(1-\theta)\left[1 + \frac{\theta \cdot (E_f \cdot \mu_m - E_m \cdot \mu_f)}{E_f\theta + E_m(1-\theta)}\right].$$
(10.11)

Strength properties of UD-composite

Determination of composite ultimate stress at tension (compression) and the shear requires application of the additional assumptions: preliminary residual stress in composite is absent; composite failure corresponds to loosing load-carrying ability of at least of one of its component – i.e. fibers or matrix.

Ultimate tensile (compression) strength along fibers. During the strength test it is necessary to determine what component fails earlier - fiber or the matrix. For this it is necessary to analyze the stress-strain diagrams of composite components as separate isotropic materials (Fig. 10.3, **a**).
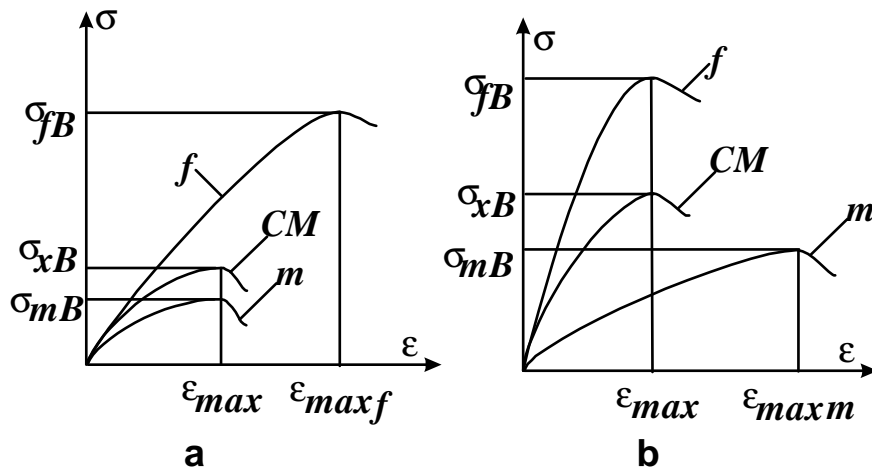

Fig. 10.3. Stress-strain diagrams of UD-composite components: **a** – maximum strain of fiber is more than maximum strain of matrix; **b** –maximum strain of fiber is less than maximum strain of matrix

While $\varepsilon_{maxm}<\varepsilon_{maxf}$ the composite ultimate strength along fibers is determined as follows:

$$\sigma_{xB} = \frac{\sigma_{mB}}{E_m}\left[E_f\theta + E_m(1-\theta)\right].$$ (10.12)

While $\varepsilon_{maxm}>\varepsilon_{maxf}$ the composite ultimate strength along fibers is determined as follows:

$$\sigma_{xB} = \frac{\sigma_{fB}}{E_f}\left[E_f\theta + E_m(1-\theta)\right].$$ (10.13)

The ultimate tension (compression) stress of composite across fibers

The more exact value of ultimate strength is obtained upon consideration of the real form of a fiber. According to the assumptions used, the strength of composite is determined with the strength of its least strong component (as a rule, it is matrix). Experimental data show that in this case the strength of composite is underestimated. Therefore, the strength of composite across fibers is more precisely can be determined according to the formula, which considers the strength of a fiber:

$$\sigma_{yB} = \sigma_{mB}\left(\frac{\pi}{2\theta} - 2\right)\cdot\left(\frac{\pi}{\sqrt{\pi^2 - 16\theta^2}}\,arctg\sqrt{\frac{\pi+4\theta}{\pi-4\theta}} - \frac{\pi}{4}\right).$$ (10.14)

Ultimate shear strength of UD-composite

The evaluation of ultimate shear strength of composite is fulfilled similarly to the evaluation of ultimate strength along fibers. In this case assumption is accepted about the identical angle displacement of fiber, matrix and most elementary section composite. For this, it is necessary to study preliminarily the diagrams of composite components testing at shear (diagram of τ-γ).

In the case of $\gamma_{maxf}<\gamma_{maxm}$ the ultimate shear strength of composite is determined as follows:

$$\tau_{xyB} = \frac{\tau_{fB}}{G_f}\left[G_f\theta + G_m(1-\theta)\right].$$ (10.15)

In the case of $\gamma_{maxf}>\gamma_{maxm}$ the ultimate shear strength of composite is determined as

$$\tau_{xyB} = \frac{\tau_{mB}}{G_m}\left[G_f\theta + G_m(1-\theta)\right].$$ (10.16)

It is necessary to note that all given in this lecture formulas are suitable for the preliminary estimation of composite properties. They give satisfactory convergence with the experimental data while θ =40...70%. It is necessary to

use experimental data during the structural strength estimation.

Checking-up questions

1. Analytical model of UD-composite.
2. Main elastic constants of UD-composite.
3. Physical (Hook's) law for UD-composite.
4. The rule of mixture for determination composites physical and mechanical properties.
5. Determination elasticity modulus of UD-composite.
6. Determination shear modulus of UD-composite.
7. Determination strength of UD-composite.
8. Determination linear expansion and shrinkage coefficients of UD-composite.

Theme 11. VARNISH-AND-PAINT PROTECTIVE COATINGS

Paintwork materials are multicomponent compositions, capable during the deposition by thin layer on the surface of an article to dry with the formation of film held down by adhesive forces. Film can be transparent, semi-transparent or have definite color.

The most important components of paints are film-forming materials, solvents and pigments. Furthermore following components can be added to paints and varnishes: plasticizers, fillers, desiccants, catalysts, hardeners, initiators and polymerization accelerators, emulsifiers, components for an improvement in the wetting and spreading on surface etc.

Film forming materials may be subdivided into thermoplastic and thermosetting.

Pigments impart to film the color, spreadability, increase its strength and performance properties. The organic pigments, which impart beautiful bright tones to coatings, gain the increasing value.

Fillers are added for the reduction of prices of paints, and also for improvement strength and protective properties of coatings. They are natural products. They include the chalk, kaolin, barite, talc, kieselguhr, etc. Some fillers are introduced for increasing the heat resistance of coatings, for example mica and asbestos.

According to composition and designations all polymeric protective coating are subdivided into the varnishes, the ground works, the putties, the paints (including of enamel).

Varnishes are the solutions of film forming materials in the organic solvents. They are used for obtaining transparent coatings or depositing the surface layer after the layer of enamel for increasing luster of a coating.

Primings (ground works), putties and paints are the pigmented varnishes or drying oils (drying oils with the addition of catalyst of the process of drying). The paints, manufactured on the varnishes, are called enamel paints or enamels, and those manufactured on the drying oil - by oil paints.

Primings are used for depositing the prior layers of the coatings, which ensure strong adhesion with the painted surface and possess good anticorrosive properties. Following primings are widely used for aircraft structures protection: ГФ-020, ГФ-032ГС, ФЛ-03-К, ЭП-09Т, ГФ-031, ФЛ-О3-Ж, ФЛ-086, АК.-069, АК.-070, ВЛ-02, ВЛ-08, ВЛ-023.

Putties are used for the smoothing of surface; they have high viscosity, considerably higher than remaining paints. The adhesion of putties to the metal is low; therefore they will be applied on the primings.

Enamels are used for obtaining the upper layer of coating over layer of priming or putty. They give durability and color to coating.

Designation of paints and varnish coatings. Designation and name of a coating consists of the words, letters and numbers may be conferred to each paint:

1-st group - kind of the paints, designated by word - varnish, paint, enamel, priming, and putty;

2-nd group - type of the filming substance (resin, ether of cellulose, etc.), designated by two letters;

3-d group - operating conditions of paints, designated by one number (1, 2, and so on.);

4-th - ordinary number, conferred to each paints, designated, one, by two or three numbers;

5-th - color of enamel, paint, putty or priming, designated by complete word, and in the special cases with the addition of ordinal number.

Examples of the designations of paint and varnish coatings

Varnish bituminous (БТ) electrical insulating - varnish БТ-99.

Enamel nitrocellulose (**НЦ**) red, for coloring the metallic and wooden articles, operated indoors - enamel **НЦ-25** red.

Ready-to-use paints and varnish coatings must possess high water resistance, long service life, hardness, elasticity, and also good adhesion to the painted part.

For colorizing metals predominantly varnish and oil, glyptal, pentaphthalic or perchlorovinyl paints are used. Drying vegetable oils, synthetic and natural resins, mineral pigments and some other substances can enter into their composition.

The convertible and non-convertible paints are distinguished. In the convertible paints solid film is formed as a result of the physicochemical processes, which occur in oils in the course of time. In the non-transformable paints this film is created as a result of the evaporation of volatile solvents.

Paint and varnish coats frequently have complex structure. Directly prime coating will be applied to the part, then for the smoothing of surface - putty, enamel and finishing varnish further follow.

The prime coating which is contacted with the metal, must possess high anticorrosive properties and ensure a good adhesion of entire varnish-and-paint film with the surface of an article.

One of the universal coating is the varnish and oil prime coating АЛГ-1, which creates the protective passivating medium, which contains chromate salts.

The quick-drying acrylic prime coating АГ-10с based on the strontium crown as the pigment has high adhesive properties with respect to the unoxidized surfaces of magnesium alloys.

Glyptal primer 138A pigmented by the Indian red is frequently used during coloration of parts made of aluminum alloys and steels for the best adhesion, applied directly to the metal, with the perchlorovinyl and nitrocellulose enamels. During the coloration of magnesium parts the glyptal primer АЛГ-7 is widely used.

One should underline that pigments, which contain lead (the red lead oxide, chrome yellow) introduced into some prime coatings can form the sub-

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stances in the presence of moisture, which possess cathode functions with respect to Al and Mg. Thus they facilitate the electrochemical destruction of these metals; therefore such prime coating cannot be recommended for coloring the parts from the aluminum and magnesium alloys.

For smoothing of the undercoated surfaces heavy-bodied pastes, i.e. putties are used. The necessary viscosity is achieved by the introduction of fillers into them (for example, chalk, talc, kaolin etc). Varnish and oil putty AM and perchlorovinyl putty ХВШ-4 are most widely used during the coloration of metal parts.

There are many grades of enamels, developed for hardware colorizing. It is possible to distinguish the groups of perchlorovinyl (ХВЭ), glyptal (А-6ф…А-15ф), varnish and oil (А21м, А21г etc.), silicone (К-1, К-2) enamels, nitrocellulose enamel (ДМ) and some others.

Coloration of out-door parts requires one or two layers of the perchlorovinyl enamel of the desired colore; the films of such enamels are characterized by high strength and elasticity, water resistance, weather resistance and incombustibility. However, their adhesive properties are low and the strong adhesion of a film with metal is achieved by the application of the corresponding prime coatings.

Instead of the complex coating 1-2 layers of varnish 9-32, which is the solution of polybutylmetacrylate dissolved in organic solvents may be applied to some out-door parts. This varnish possesses a good adhesion to the metals and is characterized by high weather resistance. Based on this varnish the enamel of 9-32ал is manufactured, which contains as the pigment aluminum powder.

For colorizing parts of aircraft engine, which are heated in the work up to high temperatures, for example heat and exhaust ducts, combustion chambers, and in certain cases even blades of turbines and nozzle cascade, the special high-temperature (oxidation-resistant) enamels are used. These enamels prevent gas corrosion and the erosion effect due to flow of hot gases.

The application of anti-corrosive methods of protection depends on the composition of structural material and operational conditions of a part. Table 11.1 presents the methods of corrosion protection of basic aircraft parts.

Quality control of paint and varnish coatings

Quality of protective coating can be estimated by its thickness, hardness, wear- (erosion) resistance, impact-resistance, flexibility, adhesion to protecting surface.

The thickness of protective coating is measured by micrometer or with ultrasonic indenter.

Testing of paint and varnish coatings hardness is conducted by the methods of indentation (based on the Brinell and Rockwell methods), by the method of scratching (Mohs method) with the special pencil (the width of scratch on the film is measured) and by the pendulum method (the duration of

Table 11.1. Protection of the parts of aircraft from the corrosion

Alloys	Typical parts	Methods of corrosion protection
Duralumin Д16	The elements of the airframe - spars, stringers, frames, ribs. Fuselage covering, wing, tail assembly	Alloying with manganese, for the laminated articles - cladding, anodic treatment in sulfuric acid, passivation in the solution of $K_2Cr_2O_7$ or the deposition of prime coating АЛГ-1. For the skin - after anodizing the deposition of clear varnish 170A, in the heated sections - deposition of high-temperature (oxidation-resistant) aluminum enamel К-1.
Duralumin Д1	Control rods (ailerons, stabilizers, etc.)	alloying with manganese, anodic treatment, passivation in the solution of $K_2Cr_2O_7$
Aluminum alloy В95	The elements of stressed frame - profiles, units, the skin	Protection according to the methods, indicated for Д16
Aluminum alloys АМц and АМг	Manifolds for the fuel, oil, air, oxygen, hydraulic mixture. Fuel tanks, fire-fighting equipment, anti-icing system	Priming АЛГ-1 with 5% of aluminum powder, painting with the glyptal enamels of the established/installed color. The internal surface of pipes - chemical oxidizing
Aluminum alloy АК6	Control levers and control cranks (stabilizer, controls, ailerons)	The anodic treatment with the subsequent passivation in the solution of $K_2Cr_2O_7$

Table 11.1. Protection of the parts of aircraft from the corrosion (continued)

Alloys	Typical parts	Methods of corrosion protection
Magne-sium alloys ВМ65-1, МА8, МЛ5	Control levers and control cranks, units, the elements of stressed frame, flaps	Chemical oxidizing, priming АЛГ-1 и АЛГ-5, painting with glyptal or vinyl chloride enamels
Aluminum alloy В65	Rivets	Anodic treatment with the deposition of priming АЛГ-1 on the place of setting.
Steels 3ОХГСА 30ХГСНА	Attachment fittings of engine, landing gear, wing, tail unit	Parts of landing gear - phosphatizing and painting with the gray enamel А14. standard fasteners made of steel 3ОХГСА— cadmium plating and galvanizing;
	Parts of landing gear	Washer, plungers, sleeve - blueing.
	Heavy-duty bolts, nuts and other standard fasteners	Working surfaces of axes and stocks - chrome-plating

oscillations delay is estimated or the reduction of oscillations amplitude).

The tests of flexibility are carried out by two methods: painted plate is bent by the not colored side around the set of cylindrical rods of different diameter (from 25 to 50 mm) and by the method of the indentation of semi-spherical indenter into the painted plate up to the cracking appearing (the depth of indentation is measured in this case).

Test for impact-resistance is carried out via dropping to the tested material of load with the mass of 1 kg and the studying of the completeness of coating.

Determination of adhesion is carried out by the methods of grids (parallel longitudinal and lateral slots or l notches are cut by sharp knife with spacing of 1…2 mm). By quantity of peel-out square particles of a coating the degree of adhesion may be evaluated.

The determination of internal stresses/voltages is carried out by the following method. The local deformation of the test specimen, deformed by the forces of buckling, which appears in the coating, is studied. Wear (erosion) resistance is determined by relative loosing of a specimen mass after "shooting" with quartz sand particles over coating.

Resistance of protective coatings to different climatic conditions is conducted in special chambers.

Checking-up questions

1. Main functions of protective coatings.
2. Classification of protective coatings.
3. Designation of protective coatings.
4. Typical technology of protective coatings application.
   5. Methods of quality control for polymeric protective coatings.

Theme 12. STRUCTURAL ADHESIVES

Adhesives relate to the film formers and are solutions or polymer melts, and the inorganic substances, applied to the surface.

Adhesives are supplied in the form of liquids, pastes, mastics or films. The composition of glues includes the following components:

– the filming substance (mainly thermosetting resins, natural rubbers), which determines adhesive, cohesive properties and main physical-mechanical characteristics;

– the solvents (alcohols, gasoline, etc.), which create the specific viscosity;

– plasticizers for eliminating the shrinkage phenomena in the film and increasing its elasticity;

– hardeners and catalysts for the conversion of the filming substance into the thermal-stable state;

– fillers in the form of the mineral powders, which increase strength of joint and decrease the face shrinkage.

For increasing the heat resistance the powders of **Al**, **Al$_2$O$_3$**, and **SiO2** are introduced, for increasing the current conductivity – silver, copper, nickel, graphite.

Adhesive joints in comparison with other types of structural joints (bolted, riveting, welded, etc.) have a number of the advantages: the possibility of joining different materials (metals and alloys, plastics, glasses, ceramics, etc.) both between themselves and in different combinations; weather-resistance and resistance to the corrosion of; airtightness of joint; the possibility of joining thin materials; reduction of manufacturing cost, economy of mass and considerable simplification of manufacturing technology.

Drawbacks of adhesive joints are relatively low thermal resistance (up to 350 ℃), the low strength of joint under out-of-pla ne loading, necessity of thermal treatment at curing, tendency toward the aging. However, there are a number of the examples of the durable operation of adhesive joints. New adhesives based on silicon and inorganic polymers ensure the work of joint at a temperature to 1000 ℃ and above; however, majority of the m do not possess a sufficient elasticity of film.

The strength of joint depends on the phenomenon of adhesion, cohesion and mechanical coupling of film with the surface of the glued materials.

The strength of adhesion can be raised by the mechanical cohesion of the film of glue with the rough surface of material; for this frequently the surface of parts are milled or cleaned by abrasive paper before the gluing. One more very efficient method is the application of sub-layers (substrates) on joining surfaces before major adhesive application.

Nature of the adherend materials influences the process of joining. The adhesive properties of metals are different. During the joining of plastics the solution and the melt of the same plastic guarantees the best adhesion (for example, solu-

tion of plexiglass in dichlorine-ethane). If plastics are nonpolar and are not dissolved in the solvents (polyethylene, teflon-4, polypropylene), then the nature of their surface is changed mechanically and chemical.

Classification of adhesives

Adhesives can be classified according to the number of criteria. The following adhesives are distinguished:
– on the filming substance – resin based and rubber based;
– according to the adhesive properties - **general application** (can joint practically any combination of chemically different materials (glues of БФ group, epoxy adhesives)) and **special application** (for joining definite material only (rubber adhesive for joining rubber products only);
– with respect to the heating - thermoplastic and thermosetting films;
– on the conditions of hardening - cold curing and of hot curing;
– in appearance - liquid, paste and film;
– according to the purpose – structural load-carrying and non-load-carrying.

More frequently classification on the film-forming substance is mentioned. Resin glues can be thermosetting and thermoplastic. Thermosetting resins give the strong heat-resistant films, used for the gluing of load-carrying structures made of the metals and the non-metal materials. Adhesives based on thermoplastic resins have low strength characteristics, especially during the heating, and they are used for the non-load-bearing connection the non-metal materials.

The rubber adhesives, in which the natural rubber is basic film-forming substance, are characterized by high elasticity; they are used for gluing of rubber with rubber or rubber by metals.

Structural resin adhesives

Thermosetting resins are used as the filming substances of this group of adhesives. They are hardened in the presence of catalysts and hardeners at room or elevated temperature. Adhesives of cold (room temperature) curing possess insufficient strength, especially at high temperatures. Complete hardening of resin occurs with the hot gluing, glue joint gains strength and thermal stability. The basic forms of glues can be obtained on the basis of pure resins, but taking into account that resultant with the gluing resin is brittle, resin is combined with the natural rubber, thermoplastics, etc.

Adhesives based on modified phenol-formaldehyde resins

These glues are used mainly for the joining metal load-bearing structural

elements, for example, made of glass-fiber-reinforced plastics, etc.

Phenolic rubber compositions are elastic heat-resistant films with the high adhesion to the metals. Adhesive joints are heat-resistant, can withstand well to cyclic loads, the strength of joint under the non-uniform loading is ensured because of the elasticity of film. Adhesives are water-resistant and can be utilized under different climatic conditions.

Phenolpolyvinylacetale compositions most widely are utilized in the glues БФ. They are used for the joining metals, plastics, ceramics and other solid materials. The thermal stability of adhesive joints is low, water resistance satisfactory.

Phenolorganicsilicon adhesives contain asbestos, aluminum powder, etc as the fillers. They have high resistance to high temperature, water and the tropical climate, they possess a good resistance to vibration and high shear strength.

Adhesives based on epoxy resins. Hardening of such kind of adhesives occurs in presence of hardeners (catalysts) without the release of by-products, that decrease the shrinkage phenomena in the glue film (shrinkage coefficient is 3…5%).

Curing of resin can be conducted both by cold and hot method. Epoxy adhesives of hot curing are structural load-carrying adhesives.

Polyurethane glues. The glues of cold and hot hardening are produced. They possess general purpose adhesion, resistance to vibration. Their deficiency is toxicity.

Glues based on silicon compounds. They possess high thermal stability. Adhesive properties are low; therefore, these glues are used in combination with other resins. Adhesives ВК-8, ВК-2, ВК-15 are cured at high temperatures. They are used for joining steels, titanium alloys, glass, asbestos fiber-reinforced plastics, inorganic materials.

Glues based on heterocyclic polymers. Examples of designation: ПБИ-1К, СП-6. They are applied for the joining metals and non-metals, in particular laminated plastic.

Structural rubber adhesives

They are intended for the joining of rubber with rubber and for rubber-to-metal bonding, glass, etc. These glues are the solutions of natural rubbers or rubber compounds in the organic solvents. Curing is carried out at temperature 140…150℃. Strength of adhesive joint is not inferior to the strength of whole material. Adhesive joints can work at temperatures of -60…300℃.

Inorganic adhesives

They are high-temperature; supplied in the form of the concentrated aqueous solutions of inorganic polymers, in the form of solid powders, and in

the form of glue- cements or glue-paste. Phosphate, silicate and ceramic adhesives are used.

Ceramic adhesives are the fine suspensions of the oxides of alkali metals in the water. Such adhesives can be applied to the surfaces preliminary coated with substrate, they are partially dried, and then at a small pressure are heated to the melting point of components and are maintained during 15…20 min. Strength of joint is retained up to the temperature of 500…1000 ℃.

Silicate adhesives. Liquid glass possesses the gluing ability; it is possible to use it for joining glass, ceramics, glass - to metals and plastics.

The properties of adhesive joints

Adhesive joints are mostly effectively operate at shear (ultimate shear strength for adhesive joint can reach 5…50 MPa). In the adhesive joints uniform and non-uniform failure and peeling of film at the edge or welding seam can occur.

In the case of non-uniform loading the strength of joint is at least of several times less than at uniform shear loading. Under the compression, the strength of adhesives is more 5…10 times more comparing with tension.

The strength of adhesuin depends substantially on the temperature. The form of glue and the nature of the stressed state exert great influence. Poisson ratio of glue $\mu = 0.3$; the shear modulus $G = 0.38\ E$; the module of elasticity $E = 2…4$ GPa; the elongation at rupture of the hardened layer is approximately 3.5 %.

The thermal stability of glues is different. Phenolic rubber and epoxy glues can operate durably (up to 30 000 hrs) at a temperature of 150℃ and above it. Poly-aromatic and organic-metal adhesives withstand temperature 200…400 ℃ during 2000 hrs.

Under operating conditions and during the storage of adhesives the embrittlement of adhesive material begins. This phenomenon flows the more rapid at higher temperatures.

Durability (number of cycles before failure) depends on the adhesive form. Average life-time of adhesive joint at cyclic loading is $10^6...10^7$. The resistance of adhesives joints to prolonged action of loads can be increased with the reinforcement of adhesive film by fibrous fillers.

Joining of the laminated composite wing skins, fuselage, tail unit in the Kharkov Aviation plant is manufactured by adhesives BK-25, BK-41, BK-51. The glues are supplied in the reels (glue films). Producers are - Kazan, Shostka (Russia). Glue BK-25 is rubber, of red color. Operating temperature is -60…+150℃. Glue BK-41 is epoxy, transparent. Glue BK-51 is rubber, of blue color. Operating temperature is -60…+80 ℃.

The physical-mechanical properties of structural resin glues are given in Table 12.1.

Table 12.1. Physical-mechanical properties of structural resin adhesives

Adhesive	Ultimate strength, MPa			Heat stability, °C	Water resistance (comparative)	Temperature of curing, °C
	At shear	At uniform abruption	At non-uniform abruption			
Phenol-formaldehyde	13...15	–	–	60...100	good	20 or 50...60
Phenolrubber	14...25	17...20.	3...5	200...350	excellent	165...205
Phenolpolyvinylacetale	17...18	36...60	0.8...1.2	200...350	good	180
Phenolpolyvinylbuterale	22	32...35	3.0	60...80	satisfactory	120...140
Phenolorganosilicon	12...17	28...30	...	250...600	good	180...200
Epoxy	10...30	10...60	1.0...1.5	60...350	satisfactory	20 or 80...210
Polyurethane	11...20	22...35	2.5...3.0	60...100	good	18...25 or 105
Polyurethane carborane-containing	10...20	24	–	350...1000	good	150
Silicon	9...17.5	15...22	0.8...2.0	350...1200	satisfactory	180...270
Polybenzimidazole	15...30	28	...	350...540	excellent	150...400
Polyimide	15...30	33	...	300...375	excellent	180...260

Example problem 12.1.

Two flat panels were jointed with adhesive according to single-lap joint scheme (Fig. 12.1). Average shear strength of adhesive τ_b at room temperature is 25 MPa. Dimensions of smaller article are: *a*=20 mm, *b*=35 mm. Calculate maximum in-plane force P mentioned joint can withstand. Shear stress distribution in adhesive layer is assumed to be uniform.
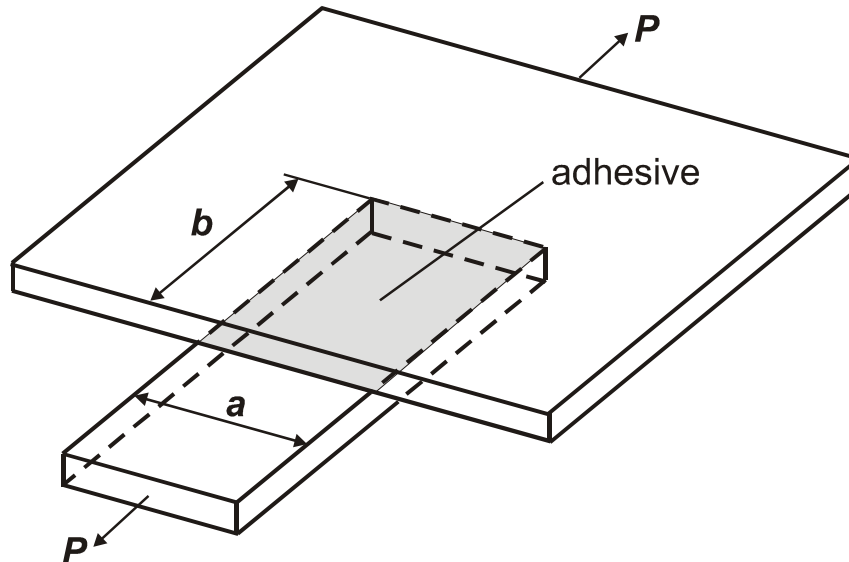

Fig. 12.1. Single-lap adhesive joint loaded with shear

Force **P** is equal to: area of contact **a·b** multiplied to average shear strength of adhesive (τ_b=25 MPa). Then **P**=17500 N (~1750 kg).

Checking-up questions

1. Definition of structural adhesive.
2. Classification of structural adhesives.
3. Main components of structural adhesives.
4. Technology of structural adhesives preparation and application.
5. Application of structural adhesives in aeronautical structures.
6. Properties of structural adhesives.
7. Universal and special structural adhesives.
8. Range of operational temperatures for structural adhesives.
9. Advantages and disadvantages of adhesive joints and joints with mechanical fasteners.
10. Testing of adhesive joints.
11. Distinctions of adhesive joint loading.

Theme 13. SEALING COMPOUNDS

Sealing compounds are used for **packing** and **hermetically pressurizing** of riveted, welded and bolt joints, fuel compartments and tanks, different metal structures, tools, units.

Requirements to the sealing compounds. Sealing compounds have possess high adhesive properties to the hermetically sealable materials, elasticity, oil -, fuel- and hydro-stability, resistance to the action of temperatures from -60 to +350℃, and be simple in the manufactur e and operation.

Sealing compounds can be classified as **static** or **dynamic**, depending on whether it occurs or there is no displacement of the hermetically sealed parts relative to each other. Shaft which rotates in the housing, is an example of typical dynamic system. If flange joints are static systems, they are subjected to small "micro-movements" because of vibration, changes in the loads, shocks, jolts, temperature changes, transmission of loads, etc.

According to purpose and operational conditions **weatherproof**, **water-resistant**, and oil and **fuel-resistant** sealing compounds are distinguished.

According to the nature of adhesion in a joint there are the **surface** and **intraseam** sealing materials. Surface sealing compounds are used in the form of paste and viscous solutions and will be applied as the sealer between the combinable surfaces of parts. Intraseam sealing compounds are used in the form of paste, tapes, tows or viscous fluids, which fill the leakages of joints.

According to the degree of adhesion to the hermetically sealable surfaces the sealing compounds can be divided into **directly applied** to the surface (with the high degree of adhesion) and the sealing compounds **applied with the help of the padding glue films** (with a low adhesion).

According to the composition, the sealing compounds **cured at high temperatures** and at **room temperature** are distinguished.

Thiocol sealing compounds are obtained on the basis of Thiokol. Sulfur, which is included in basic molecular chain, imparts to film high gas- and water vapor impermeability. They have high adhesion to the metals, the wood, and the concrete. They are stable to fuel and oils.

Industry manufactures Thiocol sealing compounds У-30М and УТ-31. Period of the service-life of these sealing compounds reaches up to 25 years. They are used in the aviation and motor vehicle industry, in the shipbuilding, for the construction technology.

Anaerobic sealing compounds are obtained on the basis of polyacrylates. These sealing compounds are known under the names of **anaterm** and **unigerm** (or **Loctite**). During curing they do not shrink and do not require high pressures. Physical-mechanical properties of some sealing compounds are given in Table 13.1.

Table 13.1. Physical-mechanical properties of some sealing compounds

Sealing compound	Density, g/cm³	Ultimate strength, MPa	Elongation per unit length, %	Operating temperature, °C	Operational medium
Thiocol (У-30М)	1.2..1.4	2.9…3.4	300…400	-42…130	fuel-, oil
Silicon	1.0…1.8	1.5…4.5	150…600	-60…300	different climatic conditions
Fluoroelastomer	1.6…3.2	7…14	120…450	-20…250	fuel-, oil, aggressive medium
Epoxy	1.5…2.0	6…55	100…150	60…75	tropical atmosphere

The film of sealing compounds is stable to the vibration and the shocks; it can operate in the aggressive media and at high pressures, durably at a temperature from - 200 to 200 ℃, short time up to the temperature 300 ℃. The shear strength of joint in the case is 6…20 MPa.

Anaerobic sealing compounds are used for hermetically sealing the micro-defects in the welded joints, castings, stamped parts for the lock of bolts, threaded connections, hermetic sealing of manifolds, etc. A drawback in these sealing compounds is their high cost.

Silicon sealing compounds are characterized by the increased thermal stability. Their representatives are **Viksint** and **Elastosil**. Viksint is used for the surface hermetic sealing of the metallic joints, electro -, radio equipment, for the intraseam riveted and welded joints; it can work in a range of temperatures from -60 to 250 ℃; it is stable under different cl imatic conditions and withstand vibration and impacts.

Elastosil is used for hermetically sealing of metals, organic and silicate glasses, ceramics, concrete; water-, heat-, and atmosphere-resistant at a temperature from -60 to 200 ℃. Elastosil is dielectri c.

Epoxy sealing compounds can be of cold curing and of hot curing; they operate in the conditions of tropical humidity, with the vibration and impact loads and used for hermetically sealing the metallic and glass-plastic articles. Sealing compound УП-5-197С is applied in the shipboard designs, УП-6-103 - in the mine equipment, УП-5-105-2 - in the electro-radiotechnical articles, УП-5-122АТ is stable to fuel and oils. The sealing compounds of cold curing can operate durably at a temperature from -60 to 75 ℃, hot curing compounds - at temperatures from -60 to 140 ℃.

Fluoroelastomer sealing compounds are heat-, oil -, and fuel-resistant, they opearte in the aggressive media. Low- and medium molecular natural rubbers serve as their basis (Ф-4Д, СКФ-26, etc.); they have the extremely high sealing properties, acid- and vapor-resistance. They can operate continuously

at temperature 250℃, and 100…200 hrs at temperatur e of 300℃; they are incombustible. Commonly the compounds СКФ-260НМ, СКФ-260НМ-2 are used. Drawbacks in these sealing compounds are unsatisfactory frost resistance (up to -22℃ only), although they are not cra cked at the temperature to 60℃, furthermore, they are unstable to the majorit y of brake fluids; it is insufficiently plastic, they have high cost. Fluoroelastomer sealing compounds find basic use in the motor vehicle and aircraft industry.

Typical **polyurethane** sealing compound is Vilad-13-2M, **polyester** - ПН-33. Properties of the sealing compound: σ_B = 10…15 MPa, σ_{Bend} = 15…21 MPa.

Packing sealing compounds are materials placed between two mating flanges for preventing the disturbances of seal. Packing compounds prevent the leakage of liquids or gases, forming the impermeable barriers. It is necessary that the packing in the long period would remain unimpaired and would not give leakage. Consequently, sealing material must be stable to the effect of liquids and/or gas-tight; it must withstand operating temperatures and loads, by which it undergoes.

There are three types of the flanged sealers:

• **standard cut packing**, manufactured from the paper, rubber, cork, metal and other materials;

• **formed on the spot packing** which is applied in the form of liquid sealer to one of the flanged surfaces directly before the assembly of parts. At the moment of parts assembling a sealer is distributed between the flanges, filling clearances, cavity, scratches and the surface irregularity. The packing is solidified after the assembly of parts and the sealing layer is formed;

• **solidified on the spot packing** is applied in the form of liquid with the help of the dosing installation by fillet to one of the flanges. Then the preliminarily applied layer of sealer is hardened under the effect of ultraviolet radiation, forming polymeric material on the flanged surface. Hermetic sealing is achieved by compressing the hardened packing at the moment of the assembly of flanges.

Selection of the type of the sealing composition depends on many operational factors. The packing solidified on the spot ideally are suitable for hermetically sealing the joints, which need frequent disassembly, or in cases when packing must be joined with the flange, since the common cut packing can be displaced during the assembly of joints. The packing forming on the spot can be used almost for any types of flange joints.

Cold curing silicone packing sealants are attached to part surfacet by the adhesion of adhesive (without pressure applied) therefore it is necessary to install joining parts before the outer layers of a sealant will begin to be polymerized. Adhesion has be retained even the displacement of flanges relative to each other in the process of operating the joint happens. During the motions of flanges silicone product is extended, and stress on the line of joining increases. If stress on the line of joint exceeds the adhesive force or cohesion of sealing

compound, hermetic sealing is failed.

The quality of surface finish is very important for the reliable hermetic sealing of joint. The contaminated surfaces reduce adhesive force, decreasing the bond strength. The cycles of thermal effect and/or large loads can delaminate the hardened sealant from the contaminated surfaces.

The evaluation of the physical-mechanical properties of sealing compounds, their period of service, service life, thermal stability, light- , ozone resistance and the methods of properties control in the process of operation are fulfilled analogously with the methods, examined during the study of paint and varnish coats.

Checking-up questions

1. Definition of sealant.
2. Classification of sealants.
3. Distinctions of sealants application.
4. Mechanical properties of sealants.
5. Recommendation of proper sealant selection.
6. Application of sealants in aeronautical structures.

Appendix A

Specific cost of typical non-metal structural materials

Material	Specific cost, $/kg
Polyvinyl chloride	0.9…1.3
Polyethylene	1.0…1.4
Polypropylene	1.3…1.8
Polystyrene	1.5…2.0
ABS plastic	2.0…3.0
Epoxies	1.5…5.0
Polyesters	1.8…4.0
Acrylics	2.3…3.0
Nylons, Acetal, Cellulosics	1.9…2.8
Polyimide	16…20
Polyphenylene oxide	6.0…8.0
Polysulfone	12…15
Polyamaide	30…35
Silicones	35…40
Fluoroelastomers	45…55
Structural SiO_2 glass	3.0…10
Structural ceramics	from 50
Glass-seramics	5.0…30
Natural Rubber	2.0...5.0
Glass-epoxy plastic	3.0…6.0
Carbon-epoxy plastic	60…250
UD Boron-aluminum	10…150
Organic-epoxy	40..120
Epoxy adhesive	3.0…8.0
Silicon sealant	3.0…15

Appendix B

Examples of application of ceramics and sitalls in aviation structures and branches of national economy
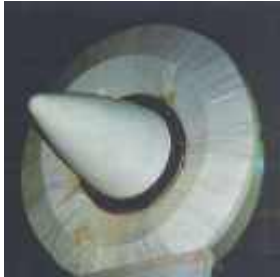
Nose cones or rockets
and pitcocks of jet engines

Blades of jet engine compressor
and turbine

Separator and rings of ball
and sliding bearings

Panels of bullet- and shell-proof armor

Inserts to channel of liquid
metals melting

Sparking plugs of engine

Cutting tools

Capacities for substances
powdering and melting

Inserts to spinneret
for fibers drawing

Substrates of chips on motherboard

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