9. IRON – CARBON ALLOYS

Ferrous alloys – those of which iron is the prime constituent – are produced in quantities larger than any other metal. They are especially important as engineering construction materials. Their widespread use is accounted for by three factors: (1) iron-containing compounds exist in abundant quantities in the earth's crust; (2) metallic iron and steel alloys may be produced using relatively economical extraction, refining, alloying, and fabrication techniques; and (3) ferrous alloys are extremely versatile, since they may be tailored to have a wide range of mechanical and physical properties. The principal disadvantage of many ferrous alloys is their susceptibility to corrosion. A classification scheme for the various ferrous alloys is presented in Figure 9.1.

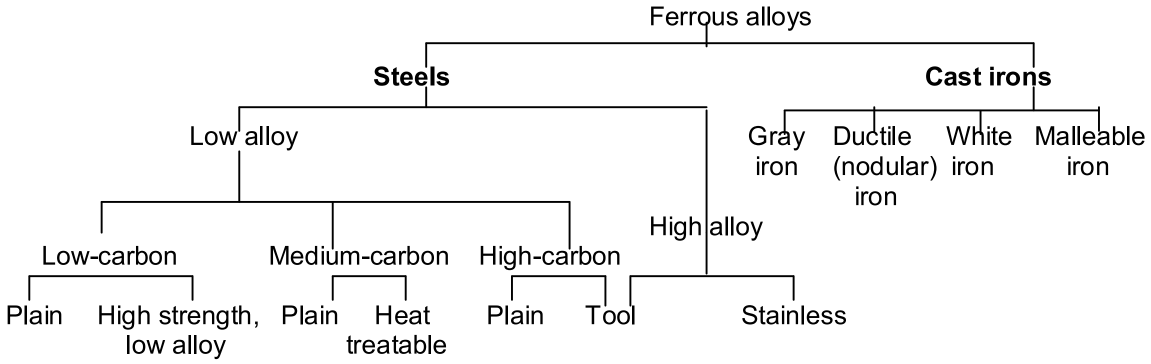


Figure 9.1 Classification scheme for the various ferrous alloys

9.1. THE IRON–IRON CARBIDE PHASE DIAGRAM

Components and phases

Components in iron–carbon alloys are a metal iron and non-metal carbon.

Iron (Fe) melts at the temperature 1539 ºC. In a solid state it experiences two polymorphic transformations. Major of them is transformation at 911 ºC. Below this temperature iron has the body-centered cubic lattice (BCC) with parameter a = 0.286 nm (see Fig. 9.2, *a*). It is referred as α iron (Fe_{α}). Above 911 ºC, the γ iron (Fe_{γ}) exists as face-centered cubic lattice (FCC) with parameter a = 0.364 nm (see Fig. 9.2, *b*).

Since α iron is ferromagnetic and high-temperature modification Fe_{γ} is paramagnetic, it is easy to identify them using magnetic methods.

High-temperature transformation γ iron to δ iron with BCC lattice influences structure and properties of alloys less, therefore it is not observed further. The designation β iron is given to paramagnetic iron with BCC lattice which exists from the Curie point (768 ºC) to 911 ºC.

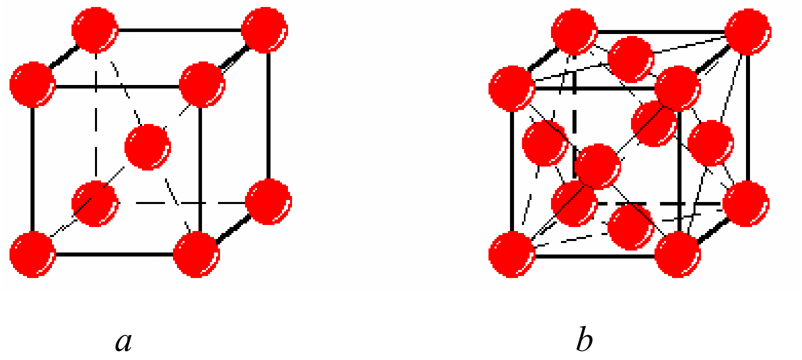

a *b*

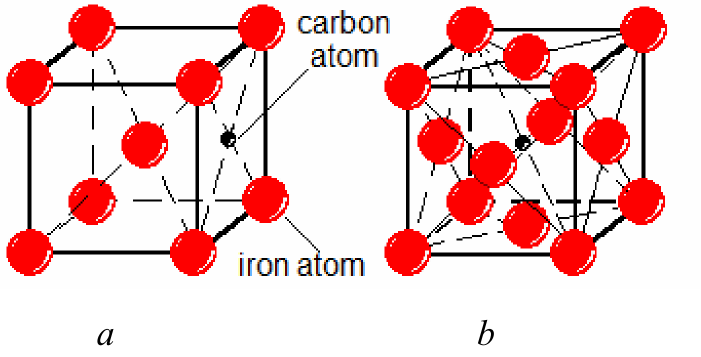
Figure 9.2 Crystal lattice of α iron *(a)* and γ iron *(b)*

Carbon (C) exists in the form of *graphite* with hexagonal layered crystal lattice under normal conditions. Carbon does not melt upon heating; it is sublimated (transfers into a gas phase) at temperature 3800 ºC. It is soft, low-strength, easily conducts electric current.

What phases may be formed by these so unlike components at interaction?

Carbon can be dissolved in liquid iron and in lattices of both polymorphic modifications; also it forms a chemical compound with iron. Therefore in the alloys following phases can exist: a liquid solution (*L*), ferrite (*F*), austenite (*A*), cementite (*C*), graphite (*G*).

Ferrite is an interstitial solid solution of carbon in α iron with limiting solubility 0.02 % wt. C. Carbon atoms are placed in defects of the iron crystal lattice, since pores of BCC lattice are too small for them (Fig. 9.3, *a*). Ferrite is soft and ductile: $\sigma_T = 300$ MPa, $\delta = 40$ %, $HB = 80\text{-}100$.



a *b*

Figure 9.3 Crystal lattice of ferrite *(a)* and austenite *(b)*

Austenite is an interstitial solid solution of carbon in γ iron with limiting solubility 2.14 % wt. C. Carbon atoms take places in the pores of FCC iron lattice (Fig. 9.3, *b*). Austenite is ductile phase, but it is harder as compared to ferrite: *HB* = 160-200, depending on concentration of carbon.

Cementite Fe_3C is a chemical compound of carbon with iron, i. e. the iron carbide containing 6.69 % wt. C. It has a complex rhombic lattice and is very hard and brittle: its hardness makes approximately 800*HB*. Cementite decomposes onto iron and carbon under a long heating above 1000 ºC. Being heated fast (by a laser beam) it melts at 1260 ºC.

Graphite is a pure carbon: soft, low-strength, chemical-resistant, well-conducting electric current.

Except for the phases mentioned above, there are two structural constituents in the structure of iron-carbon alloys: such as eutectics and eutectoid. You already know what the eutectic is. In iron–carbon system, eutectic contains 4.3 % wt. C and crystallizes at 1147 ºC. It represents a mechanical mix of austenite and cementite crystals and is called *ledeburite* (in honour of Austrian scientist-metallurgist Ledebur):

$$Ledeburite = A + C, \text{ or } Ledeburite = Fe_\gamma + Fe_3C.$$

Eutectoid is a mechanical mix of crystals of two solid phases which is formed while a solid solution decomposes (instead of crystallisation from a liquid as eutectic). In iron–carbon system, eutectoid is a mix of lamellar ferrite and cementite crystals which is formed at the expense of austenite decomposition at the temperature 727 ºC:

$$A \rightarrow F + C.$$

This mix containing 0.8 % wt. C, is called *pearlite* (because it has appearance of mother of pearl). Pearlite has the most successful combination of mechanical properties from all equilibrium structures existing in the iron–carbon alloys. Structurally pearlite is composed of soft, tough lamellae of ferrite alternating with strong, hard and rigid lamellae of cementite: $P = F + C$. Such a structure well resists to the various mechanical loadings, possesses high strength and sufficient toughness. Pearlite hardness is in the range 180-220 *HB* as depends on the grain size.

Phase transformations in iron–carbon alloys

The iron–carbon diagram looks like a combination of state diagrams considered above (see Fig. 9.4). Temperature is plotted along the ordinate, and the abscissa represents the carbon concentration in alloys, in weight percent.

Composition axis extends only to 6.69 % wt. C that corresponds to formation of a chemical compound – iron carbide, or cementite (Fe_3C). More to the right of this concentration, the diagram usually does not extend, since those alloys have no practical application. The diagram in Figure 9.5 is brought with some simplifications in comparison with Figure 9.4 and shows not the equilibrium phases only, but structural constituents in iron–carbon alloys too.

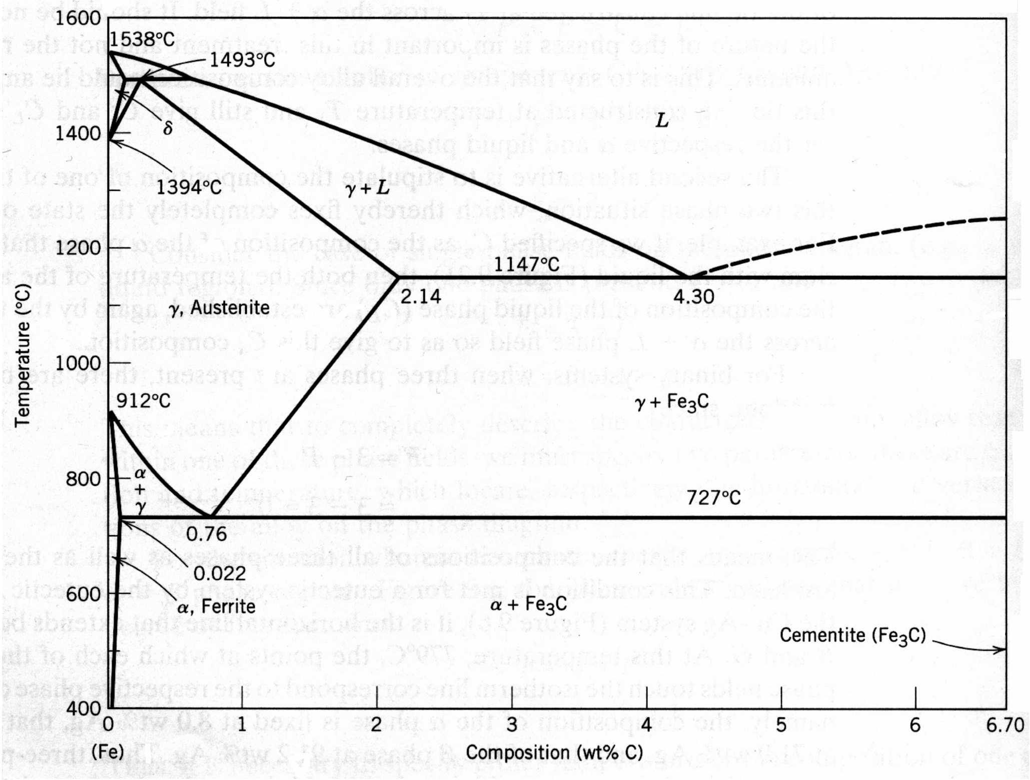


Figure 9.4 The iron–iron carbide phase diagram

Line *ACD* is the liquidus of the diagram. In the left part, under line *AC*, austenite crystallizes, and in the right one, under line *CD* cementite forms. Solidus of the diagram *AECF* consists of curve line *AE* on which crystallisation of austenite comes to the end, and horizontal line *ECF* on which eutectic reaction occurs. Upon cooling, at the temperature 1147 °C, a liquid phase is transformed into the two solid phases: austenite and cementite. This reaction may be written as follows:

$$L_{4.3} \rightarrow A_{2.14} + C_{6.7}.$$

In the alloys located to the left of point *C*, carbon content in a liquid grows in process of austenite formation, as austenite contains not more than

2.14 % wt. C. On the contrary, in alloys located to the right of point *C*, the carbon content in a liquid decreases in process of cementite crystallisation. Upon cooling to the temperature 1147 ºC the liquid solution in any alloy has eutectic concentration: 4.3 % wt. C.

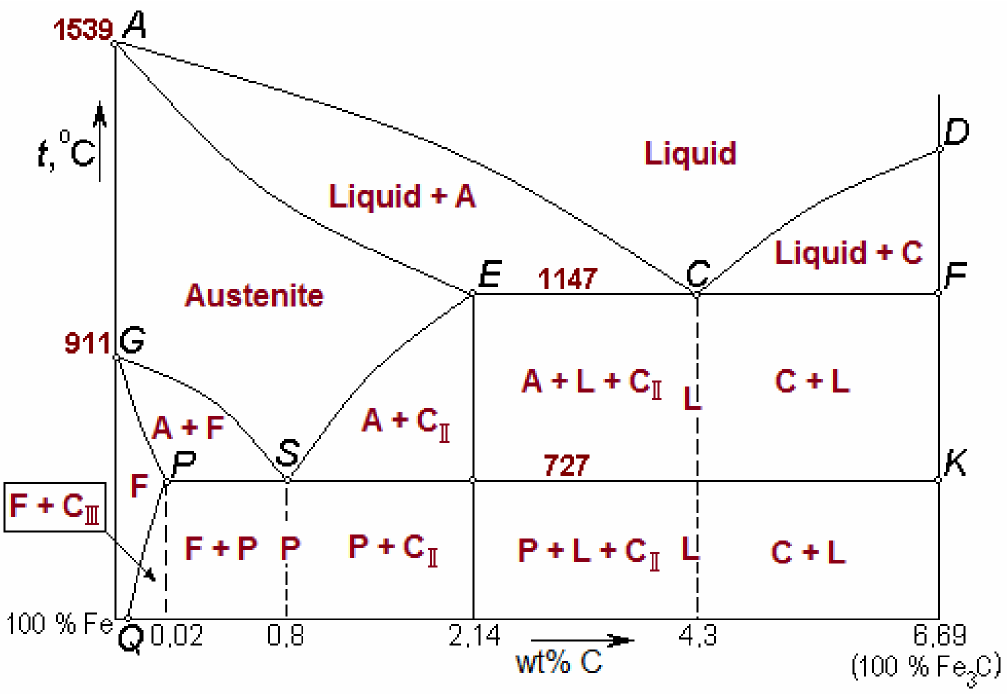


Figure 9.5 The iron–iron carbide phase diagram (simplified version)

But when the crystallisation is over, the phase transformations in iron–carbon alloys do not come to the end. Iron at 911 ºC changes the type of crystal lattice, and solubility of carbon in it decreases sharply. In the field *GSP*, two solid solutions co-exist: ferrite and austenite. Upon cooling, in the alloys containing less than 0.8 % wt. C, grains of new phase, ferrite, arise in austenite and grow until replacing it completely. Thus the concentration of carbon in austenite grows, as the ferrite almost does not contain carbon. When the temperature 727 ºC is achieved, austenite contains 0.8 % wt. C.

Besides, carbon solubility in austenite is reduced in the process of cooling. In the diagram, it is reflected by line *SE*: it is a line of limiting solubility, or solvus; below this line carbon precipitates out of γ iron lattice. But active atomic carbon immediately reacts chemically with iron, producing carbide Fe_3C. Cementite which precipitates from solid solution is called *secondary cementite*, instead of *primary* one which crystallizes from a liquid. In all alloys containing more than 0.8 % wt. C, cementite arises from austenite upon cooling. Thus, the carbon concentration in austenite decreases from 2.14 % wt. at 1147 ºC to 0.8 % wt. at 727 ºC.

So, at the temperature of eutectoid transformation (727 ºC), austenite of eutectoid concentration (0.8 % wt. C), decomposes into a mechanical mix of ferrite and cementite crystals:

$$A_{0.8} \rightarrow F_{0.02} + C_{6.7}.$$

At the normal temperature all variety of structures in iron–carbon alloys is reduced to two equilibrium phases: ferrite and cementite.

Steels and cast irons

Iron–carbon alloys long since were divided into two big groups such as steels and cast irons.

The boundary line between these two groups of alloys lies with point *E* with the carbon content 2.14 % wt. that corresponds to a limit of carbon solubility in iron. But also long before the exact methods of analysis were developed, and materials sciences foundations formulated, craftmen of melting and forging could perfectly distinguish steels from pig-iron, manufacture them and process. These alloys have absolutely different technological properties: steel can be forged, rolled, drawn down to a thin wire, but you cannot do that to the cast iron since it fractures under impact and tensile loads. But cast iron is one of the best foundry alloys, allowing make thin-walled shaped casting.

This difference in properties becomes clear when analysing the phase diagram iron–carbon. All steels (the alloys containing less than 2 % wt. of carbon) become single-phase metal when heated. This high-temperature phase is austenite, a solid solution based on FCC iron lattice. Metals having such type of crystal lattice possess the high ductility. Therefore steel is a wrought alloy.

On the contrary, the cast iron remains the two-phase metal up to the melting point, and one of these phases is hard brittle cementite, which does not allow deforming a material. But cast iron crystallizes in rather narrow temperature range, and crystallisation finishes by eutectic formation at constant temperature. It means that such alloys should have good foundry properties (high fluidity and low shrinkage) and not to form foundry defects. Therefore cast iron is a casting alloy.

It is necessary to notice that phase transformations in a solid state give possibility to strengthen steels by heat treatment. As for the cast iron, heat treatment is inefficient, because the eutectic does not change up to the melting temperature.

Also these groups of steels are distinguished by their microstructures.

Commercially pure iron is a name for alloy with carbon content below 0.02 % wt. The structure is composed of single phase – ferrite (Fig. 9.6, *a*).

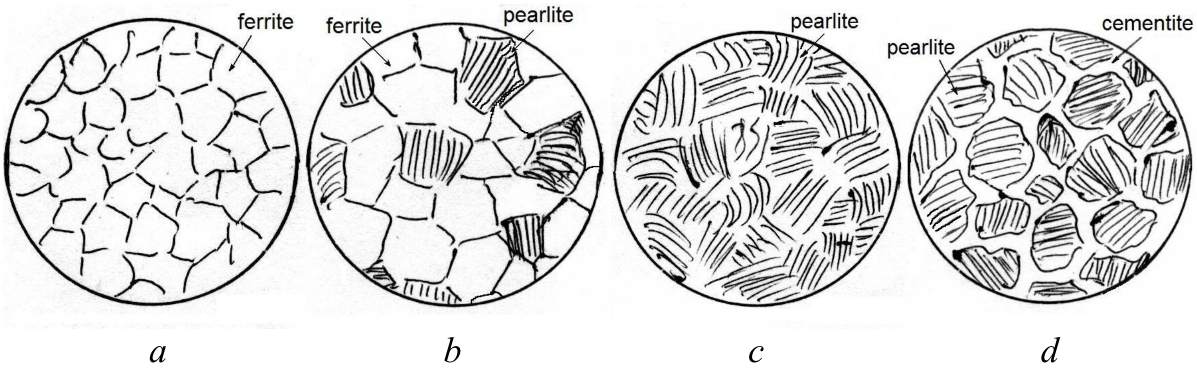


Figure 9.6 Scheme of carbon steel microstructures:
a – commercially pure iron; *b* – hypoeutectoid steel;
c – eutectoid steel; *d* – hypereutectoiod steel

1) *Hypoeutectoid steels* contain 0.02 to 0.8 % wt. C. The microstructure of alloys (Fig. 9.6, *b*) consists of ferrite (light grains) and pearlite (dark grains of lamellar structure), and the content of pearlite increases with the carbon content.

2) *Eutectoid steel* has carbon content 0.8 % wt. This steel has pearlite structure: altemating layers of ferrite and cementite (Fig. 9.6, *c*).

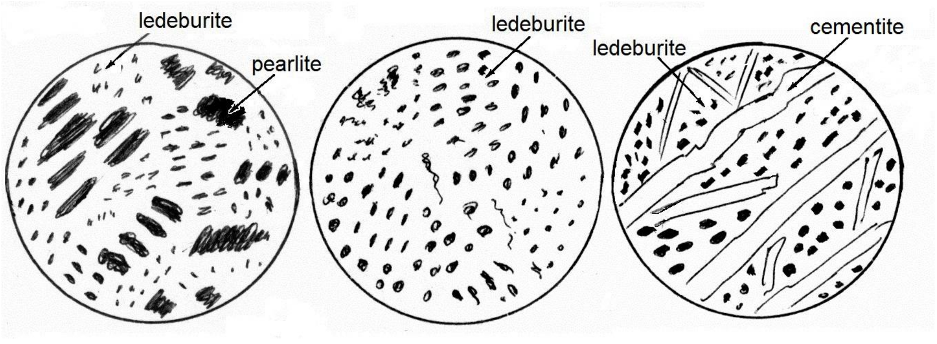
3) *Hypereutectoid steels* contain 0.8 to 2.14 % wt. C. Structurally they consist of pearlite grains, surrounded by brittle cementite network (Fig. 9.6, *d*).

Alloys represented in the right part of the diagram are *white cast iron*. They contain iron carbide, or cementite Fe_3C, instead of pure carbon, or graphite. By microstructure the following groups of white cast irons are distinguished as shown in Figure 9.7:

1) *hypoeutectic white iron* contains 2.14 to 4.3 % wt. C. The structure of alloys consists of eutectics (ledeburite) and pearlite grains;

2) *eutectic white iron* with carbon content 4.3 % wt. Alloy structure is ledeburite, consisting from cementite (a light component) and pearlite (dark grains);

3) *hypereutectic white iron* contains 4.3 to 6.69 % wt. C. The structure consists of primary cementite plates and ledeburite.



a *b* *c*

Figure 9.7 Scheme of white cast irons microstructures:
a – hypoeutectic white iron; *b* – eutectic white iron; *c* – hypereutectic white iron

9.2. PLAIN CARBON STEELS

The iron–carbon alloys that contain between 0.02 and 2.14 % wt. C are classified as ***steels***. Carbon steels make approximately 80 % of all steel production. The remained 20 % are alloy steels in which various components are specially added to provide for the enhancement of their service characteristics. Carbon steels contain only iron, carbon and a small amount of inevitable impurities transferred to liquid steel upon melting: silicon, manganese, sulphur and phosphorus.

So, *the plain carbon steels* are alloys based on iron, containing up to 2 % of carbon, and also manganese, silicon, sulphur and phosphorus in the quantities depending on a melting process.

The development of a set of desirable mechanical characteristics for steels may be achieved using phase transformation in heat treatment. For example, the tensile strength of an iron–carbon alloy of eutectoid composition (0.8 % wt. C) can be varied between 700 MPa and 2000 MPa depending on the heat treatment applied.

Carbon influence upon steel properties

Carbon is not a random impurity, but the major component of the carbon steels determining their properties.

Machine-building factories receive steel from the metallurgical enterprises either in annealed or hot-rolled states. Therefore, the as-received structure of constructional steels consists of ferrite and pearlite, and structure of tool steels composes pearlite and cementite.

The amount of cementite in steel structure increases with the increase in carbon concentration. Cementite is a very hard and brittle phase. Hardness of cementite exceeds the hardness of ferrite by a factor of 10 approximately 800*HB* and 80*HB*, accordingly. Therefore, both strength and hardness of steel grow with the increase of the carbon content; whereas both plasticity and toughness, on the contrary, decrease (Fig. 9.8).

At increase of the carbon content up to 0.8 % wt. C the share of pearlite in structure increases (from 0 to 100 %), hence, both hardness and strength grow. But at the further growth of carbon content secondary cementite appears on pearlite grains boundaries. Hardness thus does not almost increase, and strength begins to decrease because of the raised brittleness of cementite network.

Besides, the increase in the carbon content leads to increase in temperature of ductile-to-brittle transition: every tenth share of percent of carbon raises t_{50} approximately on 20°. It means that steel with 0.4 % wt. C transfers to a brittle condition approximately at 0 °C, i. e. it becomes less reliable.

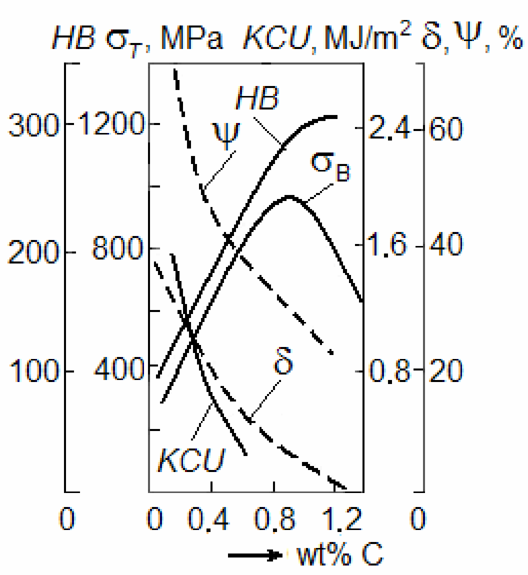


Figure 9.8 Carbon influence upon mechanical properties of steel

The carbon content influences all technological properties of steel: the more carbon concentration in steel, the more difficult it is processed by cutting, welding and plastic deformation.

Influence of inevitable impurities

Useful impurities, manganese and silicon, transfer to steel from an ingoing material – pig-iron, and also due to deoxidizing.

Manganese containing in carbon steel in quantity of 0.3-0.8 % wt., raises strength and slightly reduces toughness. It combines sulphur in sulphide MnS, that is a main advantage of manganese.

Silicon content in carbon steel should not exceed 0.4 % wt. It is dissolved in ferrite and considerably raises the yield strength. Thus worsens steel ability to cold plastic deformation: the sheet steel can give cracks upon a deep drawing.

Steel intended for cold sheet punching, is not deoxidized by silicon (ferrosilicon).

Sulphur is a harmful impurity. It causes *hot brittleness* of steel: crackling upon hot processing by pressure. It goes to steel, basically, from blast furnace fuel – a coke. Sulphur forms iron sulphide FeS, and FeS forms eutectics with melting point at 988 ºC. Steel ingots are heated up to 1200 ºC for rolling and forging. Therefore, the eutectics formed on the grain boundaries can be melted off, and ingots may be fractured.

Manganese is more active than iron when reacting with sulphur and combines it in sulphide MnS which does not form eutectics. But sulphides as any non-metallic inclusions, are concentrators of stress, reduce plasticity and toughness. Therefore the sulphur content in steel should be limited.

Phosphorus, on the contrary, causes cold brittleness of steel, shifting the onset temperature of ductile-to-brittle transition to higher temperatures. Each 1/100 percent increase in phosphorus content raises t_{50} approximately for 25º! It means that phosphorus is even more dangerous, than sulphur. Its content should be strictly limited. For decreasing the phosphorus concentration in steel it is necessary to raise the quality of fusion mixture, to apply the fluxes to remove phosphorus from the melt.

In the process of melting *gases* dissolve in steel (nitrogen, oxygen, hydrogen). They are harmful impurities also. They reduce plasticity, increase propensity to brittle fracture. Oxides are places of cracks origin. Nitrogen makes steel unsuitable for cold punching. Hydrogen causes brittleness of the tempered steel. It restores metals from oxides with water formation, and water evaporates upon heating and causes internal ruptures in metal called flakes. The gases content in steel is limited by 1/1000 of a percentage.

9.3. TYPICAL APPLICATION AND MECHANICAL PROPERTIES OF STEELS

Steels are iron-carbon alloys that may contain appreciable concentrations of other alloying elements; there are thousands of alloys that have different compositions and/or heat treatments. Their mechanical properties are sensitive to the content of carbon, which is normally below than 1.0 % wt. Some of the more common steels are classified according to carbon concentration, namely, into low-, medium-, and high-carbon types. Subclasses also exist within each group according to the concentration of other alloying elements. *Plain carbon steels* contain only residual concentrations of impurities other than carbon and a little manganese. For *alloy steels*, more alloying elements are intentionally added in specific concentrations.

Short data on the basic groups of steels given below correspond to classification of the American Iron and Steel Institute (AISI), the Society of Automotive Engineers (SAE), the American Society for Testing and Materials (ASTM), and the Uniform Numbering System (UNS).

1) Low-carbon steels

Of all the different steels, those produced in the greatest quantities fall within the low-carbon classification. *Plain low-carbon steels* generally contain less than about 0.25 % wt. C and unresponsive to heat treatments intended to form martensite; strengthening is accomplished by cold working. Microstructures consist of ferrite and pearlite constituents. As a consequence, these alloys are relatively soft and weak, but have outstanding ductility and fracture toughness; in addition, they are machinable, weldable, and, of all steels, are the least expensive to produce. Typical applications include automobile body components, structural shapes (I-beams, channel and angle iron), and sheets that are used in pipelines, buildings, bridges, and tin cans. Tables 9.1 and 9.2, respectively, present the compositions and mechanical properties of several plain low-carbon steels. They typically have yield strength of 275 MPa, tensile strengths between 415 and 550 MPa, and a ductility of 25%EL.

Table 9.1 Compositions of Plain Low-Carbon Steels and High-Strength, Low-Alloy Steels

Designation		***Composition (% wt.)***[a]		
AISI/SAE or ASTM Number	***UNS Number***	***C***	***Mn***	***Other***
Plain Low-Carbon Steels				
1010	G10100	0.10	0.45	
1020	G10200	0.20	0.45	
A36	K02600	0.29	1.00	0.20 Cu (min)
A516 Grade 70	K02700	0.31	1.00	0.25 Si
High-Strength, Low-Alloy Steels				
A440	K12810	0.28	1.35	0.30 Si (max), 0.20 Cu (min)
A633 Grade E	K12002	0.22	1.35	0.30 Si, 0.08 V, 0.02 N, 0.03 Nb
A656 Grade 1	K11804	0.18	1.60	0.30 Si, 0.1 V, 0.20 Al, 0.015 N

[a] Also a maximum of 0.04 % wt. P, 0.05 % wt. S, and 0.30 % wt. Si (unless indicated otherwise).

Another group of low-carbon alloys are the *high-strength, low-alloy (HSLA) steels*. They contain other alloying elements such as copper, vanadium, nickel, and molybdenum in combined concentrations as high as 10 % wt., and possess higher strengths than the plain low-carbon steels. Most may be strengthened by heat treatment, giving tensile strengths higher 480 MPa; in addition, they are ductile, formable, and machinable. Several are listed in Tables 9.1 and 9.2. In normal atmospheres, the HSLA steels are more resistant to corrosion than the plain carbon steels, which they have replaced in many applications where structural strength is critical (e. g., bridges, towers, support columns in high-rise buildings, and pressure vessels).

Table 9.2 Mechanical Characteristics of Hot-Rolled Material and Typical Applications for Various Plain Low-Carbon and High-Strength, Low-Alloy Steels

AISI/SAE Number	***Tensile Strength*** [*MPa*]	***Yield Strength*** [*MPa*]	***Ductility*** [*%EL*]	***Typical Applications***
Plain Low-Carbon Steels				
1010	325	180	28	Automobile panels, nails, and wire
1020	380	205	25	Pipe; structural and sheet steel
A36	400	220	23	Structural (bridges, buildings)
A516	485	260	21	Low-temperature pressure vessels
High-Strength, Low-Alloy Steels				
A440	435	290	21	Structures that are bolted or riveted
A633	520	380	23	Structures used at a low ambient temperatures
A656	655	552	15	Truck frames and railway cars

2) Medium-carbon steels

The *medium-carbon steels* have carbon concentrations in the range 0.25 to 0.60 % wt. These alloys may be heat treated by austenitizing, quenching, and then tempering to improve their mechanical properties. They are most often utilized in the tempered condition, having microstructures of tempered martensite. The plain medium-carbon steels have low hardenabilities and can be successfully heat treated only in very thin sections and with very rapid quenching rates. Alloying them by chromium, nickel, and molybdenum improves the capacity of these alloys to be heat treated, giving rise to a variety of strength-ductility combinations. These heat-treated alloys are stronger than the low-carbon steels, but at a sacrifice of ductility and toughness. Applications include railway wheels and tracks, gears, crankshafts, and other machine parts and high-strength structural components calling for a combination of high strength, wear resistance, and toughness.

The compositions of several of these alloyed medium-carbon steels are presented in Table 9.3.

Table 9.3 AISI/SAE Designation System and Composition Ranges for Plain Carbon Steel and Various Low-Alloy Steels

AISI/SAE Number[a]	*Composition Ranges (% wt. of Alloying Elements in Addition to C)*			
	Ni	*Cr*	*Mo*	*Other*
10xx, Plain carbon				
11xx, Free machining				0.08-0.33 S
12xx, Free machining				0.10-0.35 S, 0.04-0.12 P
13xx				1.60-1.90 Mn
40xx			0.20-0.30	
41xx		0.80-1.10	0.15-0.25	
43xx	1.65-2.00	0.40-0.90	0.20-0.30	
46xx	0.70-2.00		0.15-0.30	
48xx	3.25-3.75		0.20-0.30	
51xx		0.70-1.10		
61xx		0.50-1.10		0.10-0.15 V
86xx	0.40-0.70	0.40-0.60	0.15-0.25	
92xx				1.80-2.20 Si

[a] The carbon concentration, in weight percent times 100, is inserted in the place of "xx" for each specific steel.

Table 9.4 contains the mechanical characteristics and typical applications of several of these steels, which have been quenched and tempered.

3) High-carbon steels

The *high-carbon steels*, normally having carbon content 0.60 to 1.4 % wt., are the hardest, strongest, and yet least ductile of carbon steels. They are almost always used in a hardened and tempered condition and, as such, are especially wear resistant and capable of holding a sharp cutting edge. The tool and die steels are high-carbon alloys, usually containing chromium, vanadium, tungsten, and molybdenum. These alloying elements combine with carbon to form very hard and wear-resistant carbide compounds (e. g., $Cr_{23}C_6$, V_4C_3, and WC). Some tool steel compositions and their applications are listed in Table 9.5. These steels are utilized as cutting tools and dies for forming and shaping materials, as well as knives, razors, hacksaw blades, springs, and high-strength wire.

Table 9.4 Typical Applications and Mechanical Property Ranges for Oil-Quenched and Tempered Plain Carbon and Alloy Steels

AISI Number	***UNS Number***	***Tensile Strength*** [***MPa***]	***Yield Strength*** [***MPa***]	***Ductility*** [***%EL***]	***Typical Applications***
Plain Low-Carbon Steels					
1040	G10400	605-780	430-585	33-19	Crankshafts, bolts
1080[a]	G10800	800-1310	480-980	24-13	Chisels, hammers
1095[a]	G10950	760-1280	510-830	26-10	Knives, hacksaw blades
Alloy Steels					
4063	G40630	786-2380	710-1770	24-4	Springs, hand tools
4340	G43400	980-1960	895-1570	21-11	Bushings, aircraft tubing
6150	G61500	815-2170	745-1860	22-7	Shafts, pistons, gears

[a] Classified as high-carbon steels.

Table 9.5 Designation, Compositions, and Applications for Various Tool Steels

AISI Number	***Composition (% wt.)***[a]						***Typical Applications***
	C	***Cr***	***Ni***	***Mo***	***W***	***V***	
M1	0.85	3.75	0.30 max	8.70	1.75	1.20	Drills, saws; lathe and planer tools
A2	1.00	5.15	0.30 max	1.15	–	0.35	Punches, embossing dies
D2	1.50	12	0.30 max	0.95	–	1.10 max	Cutlery, drawing dies
O1	0.95	0.50	0.30 max	–	0.50	0.30 max	Shear blades, cutting tools
S1	0.50	1.40	0.30 max	0.50 max	2.25	0.25	Pipe cutters, concrete drills
W1	1.10	0.15 max	0.30 max	0.10 max	0.15 max	0.10 max	Blacksmith tools, woodworking tools

[a] The balance of the composition is iron. Manganese contents range between 0.10 and 1.4 % wt., depending on alloy; silicon contents between 0.20 and 1.2 % wt., depending on alloy.

4) Stainless steels

The *stainless steels* are highly resistant to corrosion (rusting) in a variety of environments, especially the ambient atmosphere. Their predominant alloying element is chromium; a concentration of at least 11 % wt. Cr is required. Corrosion resistance may also be enhanced by nickel and molybdenum additives.

Stainless steels are divided into three classes on the basis of the predominant phase constituent of the microstructure – martensitic, ferritic, or austenitic. Table 9.6 lists several stainless steels, by class, along with composition, typical mechanical properties and applications. A wide range of mechanical properties combined with excellent resistance to corrosion make stainless steels very versatile in their applicability.

Martensitic stainless steels are capable of being heat treated in such a way that martensite is the prime phase. Additives of alloying elements in significant concentrations produce dramatic alterations in the iron–iron carbide phase diagram. For austenitic stainless steels, the austenite (or γ) phase field is extended to the room temperature. Ferritic stainless steels are composed of the α ferrite (BCC) phase. Austenitic and ferritic stainless steels are not heat treatable; they may be hardened by cold work only. The austenitic stainless steels are the most corrosion resistant because of the high chromium contents and also the nickel additions; and they are produced in the largest quantities. Both martensitic and ferritic stainless steels are magnetic; the austenitic stainless steels are not.

Some stainless steels are frequently used at elevated temperatures and in severe environments because they resist oxidation and maintain their mechanical integrity under such conditions; the upper temperature limit in oxidizing atmospheres is about 1000 °C. Equipment employing these steels includes gas turbines, high-temperature steam boilers, heat-treating furnaces, aircraft, missiles, and nuclear power generating units. One ultrahigh-strength stainless steel (17-7PH) also included in Table 9.6 is unusually strong and corrosion resistant. Strengthening is accomplished by precipitation-hardening heat treatments.

Table 9.6 Designation, Compositions, Mechanical Properties, and Typical Applications for Several Stainless Steels

AISI Number	*Composition (% wt.)*[a]	*Condition*[b]	*Mechanical Properties*			*Typical Applications*
			Tensile Strength [*MPa*]	*Yield Strength* [*MPa*]	*Ductility* [*%EL*]	
409	0.08 C, 11.0 Cr, 1.0 Mn, 0.50 Ni, 0.75 Ti	Annealed	380	205	20	Automotive exhaust components, tanks for agricultural sprays
446	0.20 C, 25 Cr, 1.5 Mn	Annealed	515	275	20	Valves, glass molds, combustion chambers
304	0.08 C, 19 Cr, 9 Ni, 2.0 Mn	Annealed	515	205	40	Chemical and food processing equipment, cryogenic vessels
316L	0.03 C, 17 Cr, 12 Ni, 2.5 Mo, 2.0 Mn	Annealed	485	170	40	Welding constructions
410	0.15 C, 12.5 Cr, 1.0 Mn	Annealed	485	275	20	Rifle barrels, cutlery, jet engine parts
		Q & T	825	620	12	
440A	0.70 C, 17 Cr, 0.75 Mo, 1.0 Mn	Annealed	725	415	20	Cutlery, bearings, surgical tools
		Q & T	1790	1650	5	
17-7PH	0.09 C, 17 Cr, 7 Ni, 1.0 Al, 1.0 Mn	Precipitation hardened	1450	1310	1-6	Springs, knives, pressure vessels

[a] The balance of the composition is iron.

[b] Q & T denotes quenched and tempered.

9.4. CAST IRONS

True equilibrium diagram for iron and carbon

Generally, ***cast irons*** are a class of ferrous alloys with carbon contents above 2.14 % wt.; in practice, however, the most part of cast irons contain 3.0 to 4.5 % wt. C and, in addition, other alloying elements. A reexamination of the iron–iron carbide phase diagram reveals that alloys within this composition range become completely liquid at temperatures approximately 1150 to 1300 ºC, which is considerably lower as compared to steels. Thus, they are easily melted and amenable to casting. Furthermore, some cast irons are very brittle and casting is the most convenient fabrication technique.

Cementite (Fe_3C) is a metastable compound, and under some circumstances it can be made to dissociate or decompose to form α ferrite and graphite according to the reaction

$$Fe_3C \rightarrow 3Fe\ (\alpha) + C\ (\text{graphite}). \qquad (9.1)$$

Thus, the true equilibrium diagram for iron and carbon is not that presented in Figure 9.4 on page 69, but rather as shown in Figure 9.9. The two diagrams are virtually identical on the iron-rich side; however, Figure 9.9 extends to 100 % wt. carbon such that graphite is the carbon-rich phase, instead of cementite at 6.7 % wt. C.

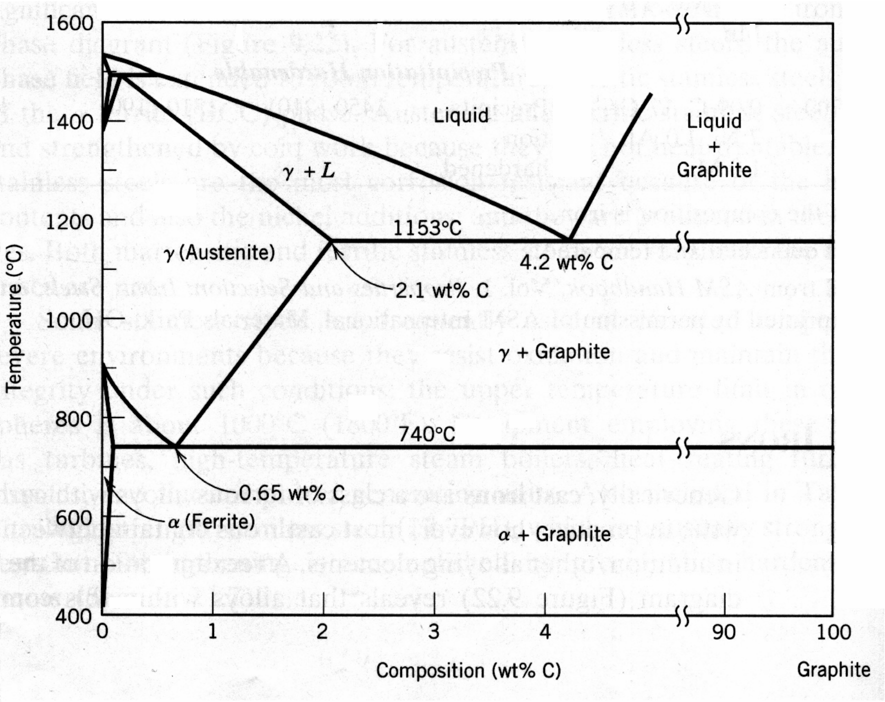


Figure 9.9 The true equilibrium iron–carbon phase diagram with graphite

This tendency to form graphite is regulated by the composition and rate of cooling. Graphite formation is promoted by the presence of silicon in concentrations greater than about 1 % wt. Also, slower cooling rates during solidification favor graphitization (the formation of graphite). For most cast irons, the carbon exists as graphite, and both microstructure and mechanical behavior depend on composition and heat treatment. The most common cast iron types are gray, nodular, white and malleable.

Gray irons

The carbon and silicon contents of ***gray cast irons*** vary between 2.5 and 4.0 % wt. and 1.0 and 3.0 % wt., respectively. For most of these cast irons, the graphite exists in the form of flakes (similar to corn flakes), which are normally surrounded by the α ferrite or pearlite matrix; the microstructure of a typical gray iron is shown in Figure 9.11, *a*. Because of these graphite flakes, a fracture surface has a gray appearance, hence its name.

Mechanically, gray iron is comparatively weak and brittle in tension as a consequence of its microstructure; the tips of the graphite flakes are sharp and pointed, and may serve as points of stress concentration when an external tensile stress is applied. Both strength and ductility are much higher under compressive loads. Typical mechanical properties and compositions of several of the common gray cast irons are listed in Table 9.7. Gray irons do have some desirable characteristics and, in fact, are utilized extensively. They are very effective in damping vibrational energy; this is represented in Figure 9.10, which compares the relative damping capacities of steel and gray iron. Base structures for machines and heavy equipment that are exposed to vibrations are frequently constructed of this material. In addition, gray irons exhibit a high fluidity at casting temperature, which permits casting pieces having intricate shapes; also, casting shrinkage is low. Finally, and perhaps most important, gray cast irons are among the least expensive of all metallic materials.

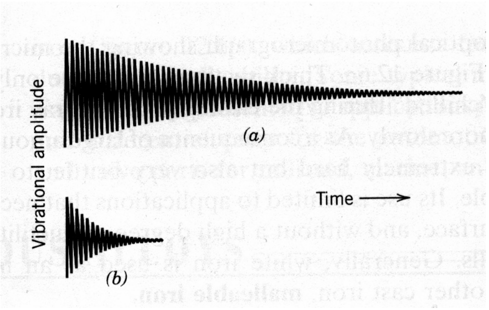


Figure 9.10 Damping capacities of steel (*a*) and gray cast iron (*b*)

Table 9.7 Designations, Minimum Mechanical Properties, Approximate Compositions, and Typical Applications for Various Gray, Nodular, and Malleable Cast Irons

Grade	***UNS Number***	***Composition (% wt.)***[a]	***Matrix Structure***	***Mechanical Properties***			***Typical Applications***
				Tensile Strength [*MPa*]	***Yield Strength*** [*MPa*]	***Ductility*** [*%EL*]	
Gray Iron							
SAE G1800	F10004	3.4-3.7 C, 2.55 Si, 0.7 Mn	Ferrite + Pearlite	124	–	–	Miscellaneous soft iron castings in which strength is not a primary consideration
SAE G2500	F10005	3.2-3.5 C, 2.20 Si, 0.8 Mn	Ferrite + Pearlite	173	–	–	Small cylinder blocks, cylinder heads, pistons, clutch plates, transmission cases
SAE G4000	F10008	3.0-3.3 C, 2.0 Si, 0.8 Mn	Pearlite	276	–	–	Diesel engine castings, liners, cylinders, and pistons
Ductile (Nodular) Iron							
ASTM A536 60-40-18	F32800	3.5-3.8 C, 2.0-2.8 Si, 0.05 Mg, <0.20 Ni, <0.20 Mo	Ferrite	414	276	18	Pressure-containing parts such as valve and pump bodies
100-70-03	F34800		Pearlite	689	483	3	High-strength gears and machine components
120-90-02	F36200		Tempered martensite	827	621	2	Pinions, gears, rollers, sliders
Malleable Iron							
32510	F22200	2.3-2.7 C, 1.0-1.75 Si, <0.55 Mn	Ferrite	345	224	10	General engineering service at normal and elevated temperatures
45006	–	2.4-2.7 C, 1.25-1.55 Si, <0.55 Mn	Ferrite + Pearlite	448	310	6	

[a] The balance of the composition is iron.

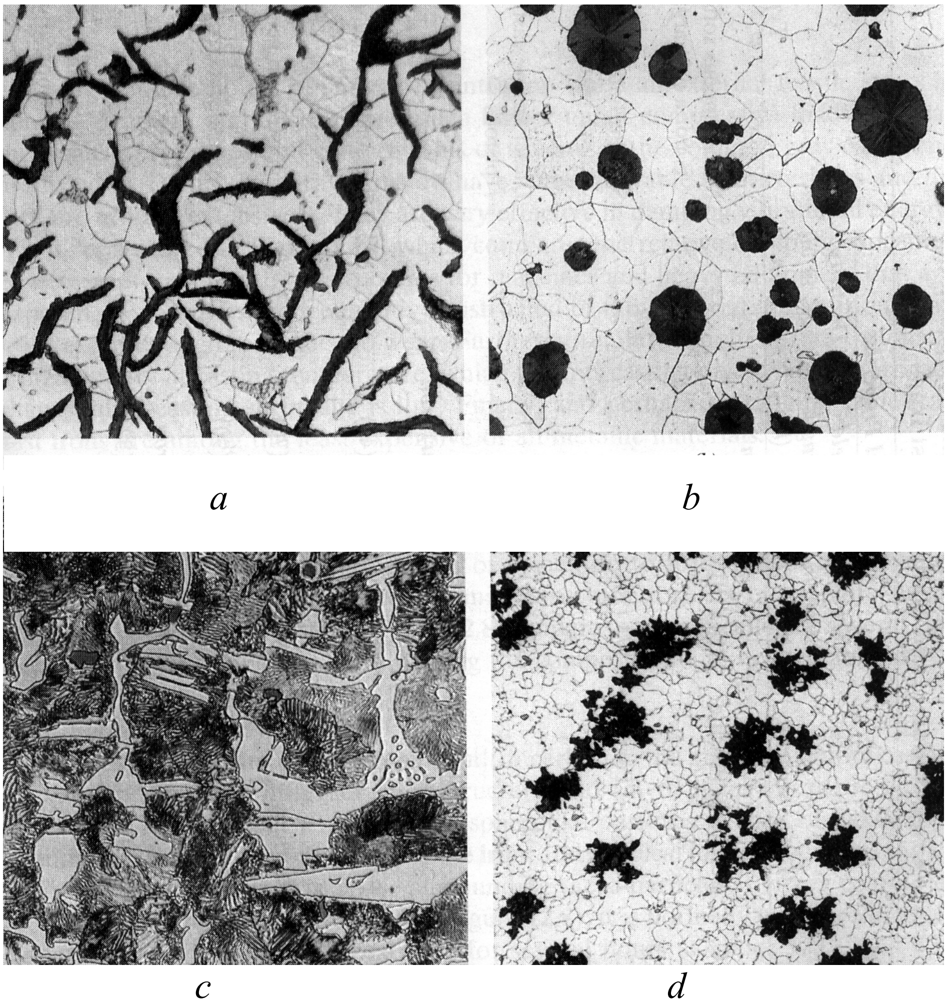


Figure 9.11 Photomicrograph of various cast irons:
a – gray iron, *b* – nodular (ductile) iron, *c* – white iron, *d* – malleable iron

Gray irons having microstructures different from that shown in Figure 9.11, *a* may be generated by adjustment of composition and/or by using an appropriate treatment. For example, reducing the silicon content or increasing the cooling rate may prevent the complete decomposition of cementite to form graphite (Equation 9.1). Under these circumstances the microstructure consists of graphite flakes embedded in a pearlite matrix. Figure 9.12 on page 86 compares schematically the several cast iron microstructures obtained by varying the composition and heat treatment.

Ductile (or nodular) iron

Adding a small amount of magnesium or cerium to the gray irons before casting produces a distinctly different microstructure and a set of mechanical properties. Graphite still forms, but as nodules or spherelike particles instead of flakes. The resulting alloy is called ***nodular*** or ***ductile***

iron, and a typical microstructure is shown in Figure 9.11, *b*. The matrix phase surrounding these particles is either pearlite or ferrite, depending on heat treatment (Fig. 9.12); it is normally pearlite for an as-cast piece. However, a heat treatment for several hours at about 700 ºC will yield a ferrite matrix as shown in this photomicrograph. Castings are stronger and much more ductile than gray iron, as a comparison of their mechanical properties in Table 9.7 shows. In fact, ductile iron has mechanical characteristics approaching to those of steel. For example, ferritic ductile irons have tensile strengths ranging between 380 and 480 MPa, and ductilities (as percent elongation) 10 to 20 %. Typical applications for this material include valves, pump bodies, crankshafts, gears, and other automotive and machine components.

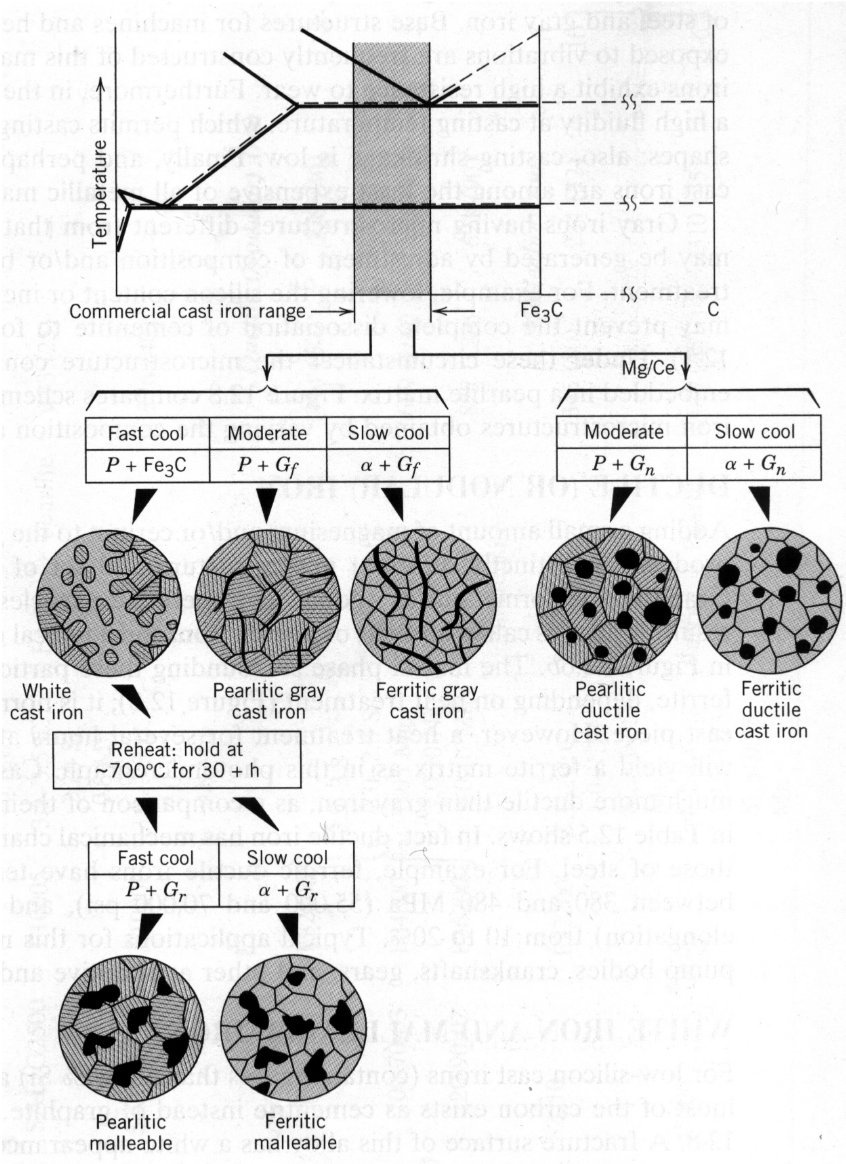


Figure 9.12 Composition ranges and microstrutures of various cast irons

White iron and malleable iron

For low-silicon cast irons (containing less than 1.0 % wt. Si) and rapid cooling rates, most of the carbon exists as cementite instead of graphite, as indicated in Figure 9.12. A fracture surface of this alloy has a white appearance, and thus it is termed ***white cast iron***. An optical photomicrograph showing the microstructure of white iron is presented in Figure 9.11, *c*. Thick sections may have only a surface layer of white iron that was "chilled" during the casting process; gray iron is formed at interior regions, which cool more slowly. As a consequence of large amounts of the cementite phase, white iron is extremely hard but also very brittle, to the point of being virtually unmachinable. Its use is limited to applications that necessitate a very hard and wear-resistant surface, and without a high degree of ductility – for example, as rollers in rolling mills. Generally, white iron is used as an intermediary production of yet another cast iron, ***malleable iron***.

Heating white iron at temperatures between 800 and 900 ºC for a prolonged time period and in a neutral atmosphere (to prevent oxidation) causes a decomposition of the cementite, forming graphite, which exists in the form of clusters or rosettes surrounded by a ferrite or pearlite matrix, depending on cooling rate, as indicated in Figure 9.12. A photomicrograph of a ferritic malleable iron is presented in Figure 9.11, *d*. The microstructure is similar to that for nodular iron, which accounts for relatively high strength and appreciate ductility or malleability.

Representative applications include connecting rods, transmission gears, and differential cases for the automotive industry; also flanges, pipe fittings, and valve parts for rail road, marine and other heavy-duty services.

Questions and problems

1. List the components and phases in iron–carbon system.
2. Analyze *phase diagram iron–iron carbide*. Show and describe liquidus and solidus, lines of limited solubility of carbon in α Fe and γ Fe, fields of solid solutions *ferrite* and *austenite*, temperature and concentration for eutectic and *eutectoid*.
3. Explain phase transformations in iron–carbon alloys.
4. What is the point in dividing iron-carbon alloys into steels and cast irons?
5. Steel *classification* by the *structure*.
6. What is the distinction between hypoeutectoid and hypereutectoid steels?
7. What are *plain carbon steels*?
8. Explain carbon influence upon steel properties.
9. What are the useful and harmful impurities in steel and what is their influence upon steel properties?
10. List the four classifications of steels. For each, briefly describe the properties and typical applications.

11. What is the function of alloying elements in tool steels?
12. Give the definitions to all types of cast irons.
13. On the basis of microstructure, briefly explain why gray iron is brittle and weak in tension.
14. Compare gray and malleable cast iron with respect to microstructure and mechanical characteristics.
15. Describe the treatment necessary to produce each of four types of cast irons.
16. What is the main performance for white cast iron?

10. HEAT TREATMENT OF STEEL

The iron–carbon alloys that contain between 0.02 and 2.14 % wt. C are classified as *steels*. The development of a set of desirable mechanical characteristics for steels results from a phase transformation, which is achieved by a heat treatment. For example, the tensile strength of an iron–carbon alloy of eutectoid composition (0.8 % wt. C) can be varied between approximately 700 MPa and 2000 MPa depending on the heat treatment employed.

The iron–carbon phase diagram presented in Figure 10.1 provides us with valuable information about the development of microstructure of the alloys. The eutectoid phase changes are very important, being fundamental to the heat treatment of steels. This eutectoid reaction may be represented by

$$\gamma(0.8\ \%\ \text{wt. C}) \overset{\text{cooling}}{\underset{\text{heating}}{\rightleftarrows}} \alpha(0.02\ \%\ \text{wt. C}) + \text{Fe}_3\text{C}\ (6.7\ \%\ \text{wt. C}). \qquad (10.1)$$

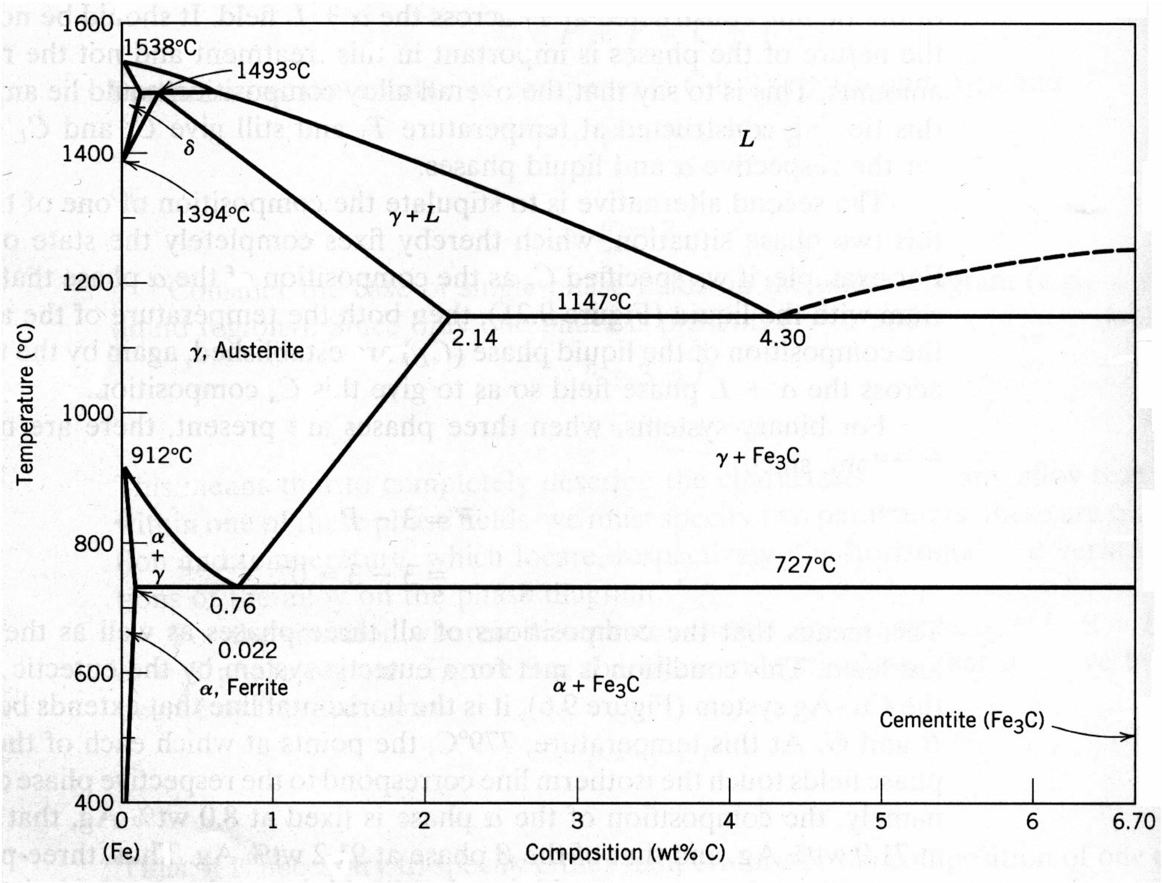


Figure 10.1 The iron–iron carbide phase diagram

It means that, upon cooling, the solid γ phase, or *austenite*, is transformed to α iron, called *ferrite*, and cementite. Upon heating, the processes develop in opposite order.

10.1. WHAT IS HEAT TREATMENT?

Heat treatment is a set of operations of heating and cooling used for changing structure and properties of an alloy in the necessary direction.

There are two types of thermal treatment: *strengthening* thermal processing, which raises hardness, strength and wear resistance, and *softening treatment*, which raises plastic properties and toughness, but reduces hardness and resistance to deformation and rupture.

Both variants of thermal processing are widely applied to steel products.

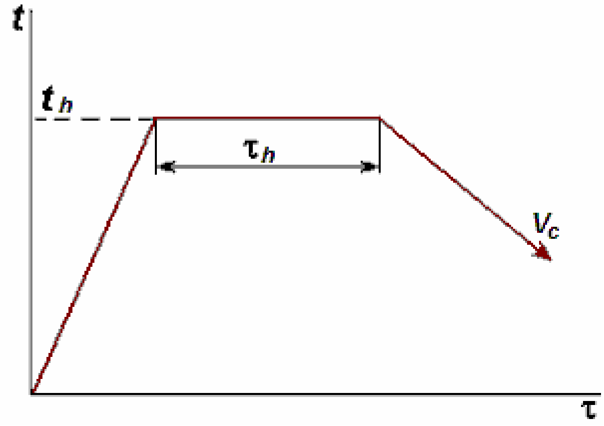


Figure 10.2 Graphic representation of heat treatment regime

It is possible to present any operation of thermal processing graphically in the form of a curve in co-ordinates “temperature – time”, including periods of heating, holding and cooling. The main parameters, defining result of thermal processing, are *heating temperature* t_h, *holding time* τ_h and *cooling rate* v_c (Fig. 10.2).

Thermal processing of steel is based on the phase transformations which occur upon heating above critical temperatures and cooling with various rates.

10.2. PHASE TRANSFORMATION IN STEELS UPON HEATING

It is accepted to designate the temperatures of transformations, or critical points of steel at heating, by following manner (Fig. 10.3):

- The beginning of ferrite – austenite transformation ($Fe_\alpha \rightarrow Fe_\gamma$) is marked as Ac_1 (these points are located on line *PSK*);
- The end of ferrite – austenite transformation ($Fe_\alpha \rightarrow Fe_\gamma$) is marked as Ac_3 (these points lie on line *GS*);
- The end of dissolution of cementite in austenite is marked as Ac_{cm} (points are on line *SE*).

Points A_2 concern to magnetic transformation, which we do not consider here.

It is necessary to note that points Ac_3 and Ac_{cm} are specific to each steel, and point Ac_1 is the same for all carbon steels: 727 °C.

Let's consider the transformations that occur upon heating of the eutectoid steel (Fig. 10.3, composition 1-1).

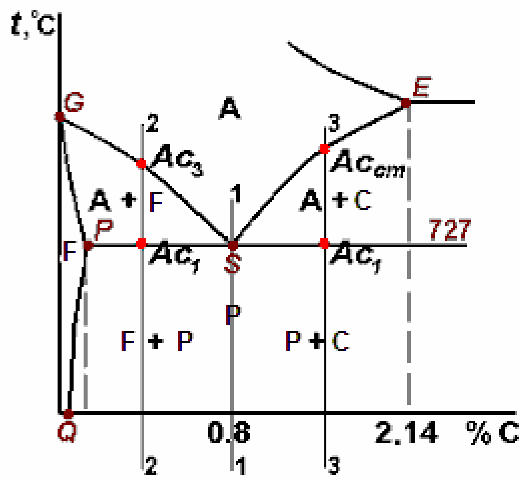


Figure 10.3 Critical points upon heating of steel

Heating from a room temperature up to the line *PSK* does not lead to any changes of structure; it remains pearlitic. When temperature Ac_1 = 727 °C is reached, transformation of pearlite to austenite begins. Nucleation of a new phase, austenite, occurs in ferrite, on the boundaries between ferrite and cementite (Fig. 10.4, *a*). The crystal lattice of iron is reconstructed from body-centered cubic into face-centered cubic: $Fe_{\alpha} \to Fe_{\gamma}$. Stimulus of transformation is a difference in free energy of a new and old phase: at the raised temperatures γ iron possesses a less storage of free energy and is an equilibrium phase. Transformation develops as diffusion process at the expense of joining new atoms of iron to a growing austenite crystal. Cementite is gradually dissolved in austenite grains.

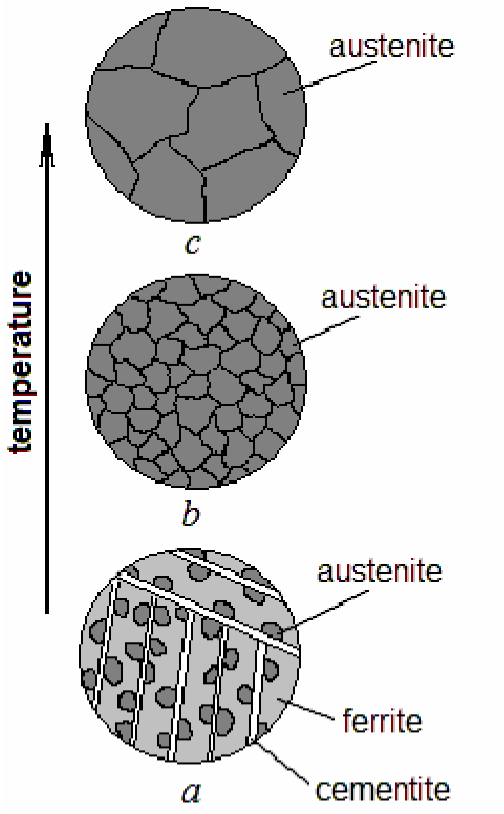


Figure 10.4 Steel structure changes upon heating

For eutectoid steel $Ac_3 = Ac_1 =$ 727 °C; it means that transformation begins and finishes at the same temperature. (Energy income while heating is spent for formation of a new surface.)

The further heating from Ac_3 to solidus does not lead to phase transformations, but with temperature increase austenite grain grows (Fig. 10.4, *b*, *c*). This process results from the fact that in coarse-grained structure the surface of grain boundaries is less therefore surface energy is less, too. The coarse-grained structure is more stable from thermodynamic point of view. Simultaneously at the expense of diffusion the carbon content in a solid solution is levelled (right after transformation former ferrite and cementite sites strongly differ in carbon concentration).

Upon heating of hypoeutectoid steels (Fig. 10.3, composition 2-2) the same transformations occur in pearlite colonies at the temperature Ac_1 = 727 °C. Then, at increase in temperature to Ac_3, surplus ferrite gradually transforms to austenite by origin and growth of grains of a new phase. The further heating is accompanied by levelling of carbon concentration at the expense of diffusion and growth of the austenite grain.

Upon heating of hypereutectoid steels (Fig. 10.3, composition 3-3) the difference is that in the temperature range from Ac_1 to Ac_{cm} a surplus cementite dissolves in austenite.

10.3. AUSTENITE GRAIN AND PROPERTIES OF STEEL

In each pearlite colony a lot of austenite grains nucleate and grow, thus leading to the refinement of steel grains upon heating. But it is important to remember that heating up to very high temperature will inevitably lead to the grain growth. It may cause two kinds of defects:

a) Overheat is a growth of austenite grain above a size, admissible under service conditions. The overheated steel has the reduced plasticity and impact strength. But this drawback can be corrected by repeated heating to normal temperatures.

b) Overburning means an oxidation and partial melting of grain boundaries at the temperatures close to solidus line. Occurrence of oxides at the austenite grain boundaries is incorrigible reject; such steel has conchoidal fracture and is very brittle. It is sent to remelting.

Grain growth upon heating occurs with different rate depending on the steel composition. In steels, deoxidized with silicon and manganese, very rapid growth of austenite grain is observed. They are *coarse-grained steels*. And steels, deoxidiezed with aluminum additionally, are *the fine-grained steels*: up to 1000-1100 °C their grains almost do not grow.

The grain size influences all mechanical properties of steel, but it especially strongly changes the impact strength *KCU*. The larger is the austenite grain before quenching, the more probable is the crack initiation after quenching. Such a steel will be less reliable in service, as compared to the fine-grained one.

The grain size is one of the major control indicators of thermal processing quality. It is estimated by a number of the scale in accordance with GOST. Metallographic method is used for comparison visible microstructure with a standard scale.

10.4. EQUILIBRIUM PHASE TRANSFORMATION IN STEELS UPON COOLING

State diagrams are developed for equilibrium condition and very slow cooling. But in practice of heat treatment cooling rate may be significantly higher. The increase in the cooling rate leads to the growth in the degree of austenite supercooling Δt i. e. the transformation of austenite begins at lower temperature in comparison with the equilibrium one. Here the same law is observed as well as for crystallization.

Overcooling degree has effect not only on the transformation rate, but on the mechanism of overcooled austenite transformation as well, therefore, on structure and properties of its products.

As a rule, cooling is carried out continuously, but it is convenient to study *kinetics* of transformations (process development in time) in *isothermal* conditions (at constant temperature). Therefore for each steel the ***diagram of isothermal austenite transformation*** is plotted in co-ordinates "temperature – time". It is called also the *C-shaped diagram* (due to the form of curves). Plotting is conducted experimentally, considering the change of any properties, usually magnetic ones. The C-shaped diagram for eutectoid steel (0.8 % wt. C) is shown in Figure 10.5.

Two curves similar to the letter "C", show the beginning (a curve *a-a*) and the completion (a curve *b-b*) of austenite transformation to other structures. To the left of the line *a-a* the field of overcooled austenite is located. As shown in the diagram, time of austenite existence at temperatures lower Ar_1 is various and it depends on overcooling degree. The minimum stability of austenite is at 550 °C: time before the beginning of transformation makes only 1 second. At 700 °C this time is equal 10 s, and at 300 °C – already 60 s. To the right of the line *b-b* the field of equilibrium products of transformation is situated.

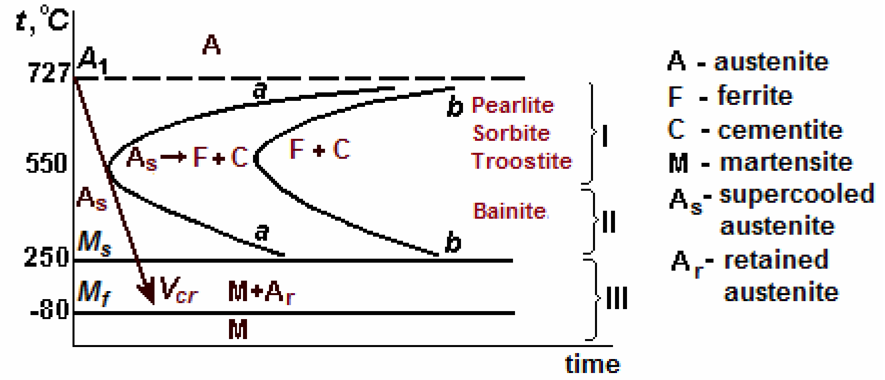


Figure 10.5 Diagram of isothermal austenite transformation for steel with 0.8 % wt. C

It means that, upon cooling, the solid γ phase, or *austenite*, is transformed to α iron, called *ferrite*, and cementite. The microstructure of the eutectoid steel slowly cooled through the temperature of phase transformation consists of alternating layers of the two phases. Both of them form simultaneously during the transformation. The composition of the parent phase is different from either of the product phases; therefore the phase transformation requires that there be a redistribution of the carbon by diffusion. Figure 10.6 illustrates schematically microstructural changes that accompany the eutectoid reaction (10.1). The directions of carbon diffusion are indicated by arrows.

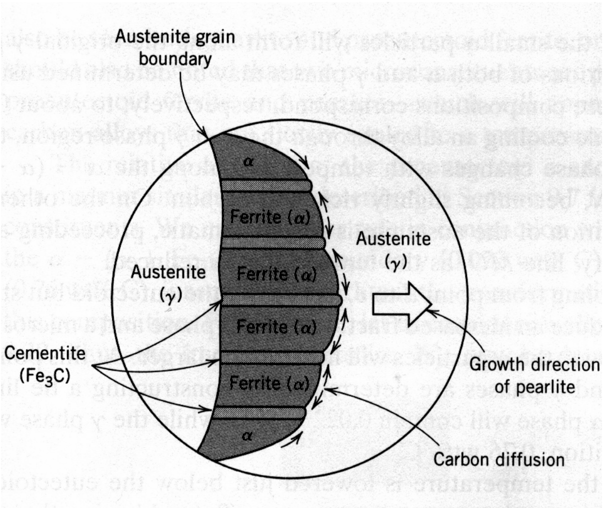


Figure 10.6 Schematic representation of the formation of pearlite from austenite

The microstructure, shown in Figure 10.7, is called *pearlite*, because it has appearance of mother of pearl. The pearlite exists as grains, often termed "colonies"; within each colony the layers are oriented in the same direction, which varies from one colony to another. The thick light layers are the ferrite phase, and the cementite phase appears as thin lamellae most of which seem dark at this magnification. Mechanically, pearlite has properties intermediate between the soft, ductile ferrite and the hard, brittle cementite.

Figure 10.7 Photomicrograph of a eutectoid steel; the pearlite microstructure consists of alternating layers of α ferrite and Fe_3C. ×500

In the temperature range 727-550 °C (Fig. 10.5, field I) process of austenite transformation develops by diffusion way at the expense of redistribution of carbon atoms in a solid solution. Natural fluctuations of carbon content in each austenite grain occur all the time, but above temperature A_1 they do not lead to phase transformations. Below critical point A_1 austenite becomes thermodynamically unstable. Therefore, as soon as in austenite grain an area with the raised concentration of carbon arises, in this site at once cementite crystal is formed. As a rule, it occurs on boundaries of grains where origin and growth of a new phase is easier due to the raised deficiency of a lattice. Atoms of carbon join a growing cementite crystal from the adjoining areas, and in these sites with lower carbon content the polymorphic transformation $Fe_\gamma \rightarrow Fe_\alpha$ occurs. Thus the nuclei of carbon-free phase – ferrite – appear.

The growing crystal of ferrite pushes away atoms of carbon which cannot occupy the places in its lattice, therefore an area enriched by carbon arises near the ferrite crystallite, where one more cementite crystallite is formed (Fig. 10.8, *b*).

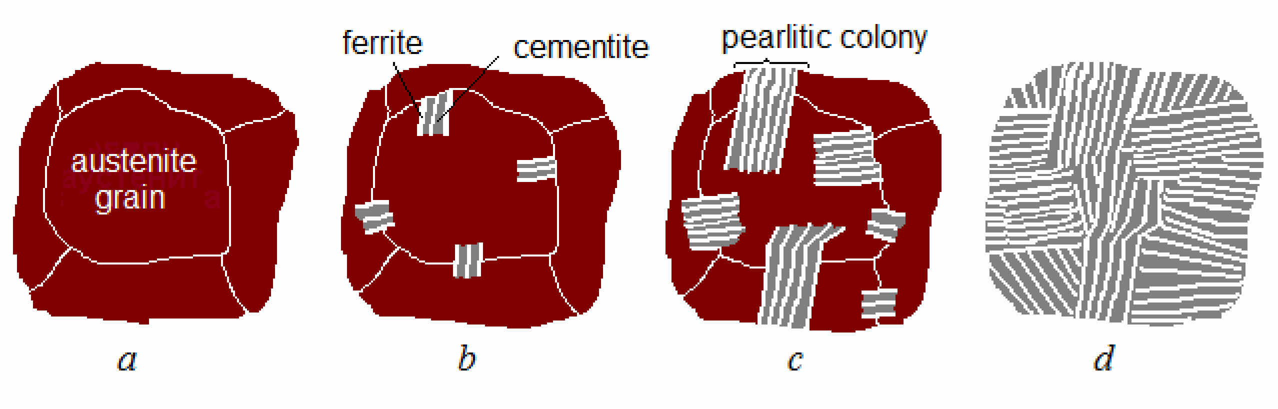


Figure 10.8 Nucleation and growth of pearlitic colonies in austenite

Forming crystals of ferrite and cementite have lamellar shape and grow parallel to each other in both sides from grain boundary. Perlitic colonies originate simultaneously in other sections of austenite grain (Fig. 10.8, *c*). Diffusive transformation develops until the initial phase – austenite – fully disappear (Fig. 10.8, *d*). It is possible to represent this process as (10.1), or as following brief expressions:

$$\text{Austenite}_{0.8} \rightarrow \text{Ferrite}_{0.02} + \text{Cementite}_{6.7}, \qquad (10.2)$$

or

$$\text{Austenite}_{0.8} \rightarrow \text{Pearlite}_{0.8}. \qquad (10.3)$$

The higher is the cooling rate, the higher is the degree of super-cooling of austenite and the more crystallites of new phase nucleate in a unit volume every second (as well as in crystallisation process). Therefore, the lower is the temperature of austenite/ferrite and cementite transformation the smaller are lamellae of these equilibrium phases. Their size is estimated by the average net width Δ of the adjacent lamellae of ferrite and cementite which is called *interlamellar distance* (see Figure 10.9).

Products of pearlitic transformation are subdivided by the grain size (or by *dispersion* of structure) into coarse and fine pearlite. Mechanical properties depend on the grain size: both hardness and strength of steel increase with the refinement of diffusion transformation products; on the contrary, both plasticity and toughness decrease (Table 10.1). The optimum combination of ductility and toughness corresponds to the interlamellar distance 0.3-0.4 µm.

As in each austenite grain a lot of pearlitic colonies arise, it is obvious that pearlitic transformation leads to steel grain refinement.

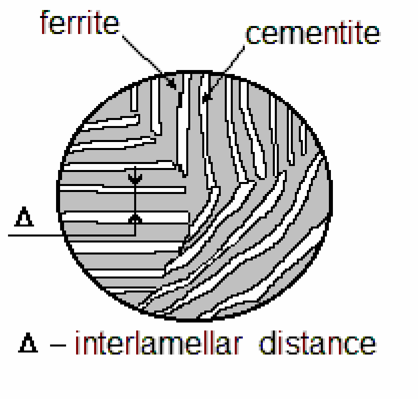


Figure 10.9 Definition of interlamellar distance

Table 10.1 Products of diffusion transformation

Structure	***Temperature of formation, °C***	***Interlamellar distance, µm***	***Hardness, HB***
Coarse pearlite	> 670	0.5–0.7	170–230
Pearlite *(sorbite)*	590–640	0.3–0.4	230–330
Fine pearlite *(troostite)*	550–580	0.1–0.2	330–400

10.5. NONEQUILIBRIUM PHASE TRANSFORMATION IN STEELS

Another type of phase transformation is developed when austenite is rapidly cooled to a low temperature.

The carbon diffusion in iron is slow down at low temperatures. At high cooling rate it is possible to cool austenite to the temperature at which diffusion practically does not take place. For eutectoid carbon steel it is approximately 250 °C. Below 250 °C, in the field III, the transformation of the supercooled austenite develops by the diffusionless mechanism (see Figure 10.5).

The horizontal lines restricting this field are marked out as M_s and M_f. M_s is the onset temperature, and M_f is the temperature of termination diffusionless transformation.

The diffusionless transformation occurs when the quenching rate is high enough to prevent carbon diffusion. In order to supercool austenite to the temperature M_s, it is necessary to reach the cooling rate exceeding magnitude V_{cr}. *Critical cooling rate* V_{cr} is a minimum value at which austenite does not transform by diffusion into ferrite and cementite mixture. Geometrically it is a tangent to the curve of the transformation beginning (line *a*-*a*).

The austenite supercooled to point M_s undergoes polymorphic transformation $Fe_\gamma \rightarrow Fe_\alpha$ which occurs without diffusion, i. e. is not accompanied by redistribution of carbon atoms. Transformation goes by *the shear* mechanism: at the expense of simultaneous displacement of all atoms in certain planes of a crystal lattice of iron to the distance less than interatomic one. Large number of atoms experience cooperative movements having only a slight displacement of each atom relative to its neighbors. It results in FCC austenite transformation to a body-centered tetragonal (BCT) crystal structure. In this case all the carbon atoms remain as interstitial impurities in iron. This supersaturated solid solution of carbon in a tetragonal lattice of α iron is called ***martensite***.

(The name is given in honour of A. Martens, German scientist.)

The crystal lattice changes and the neighboring atoms remain neighboring. All carbon dissolved in a lattice of γ iron, remains after transformation in the lattice of α iron.

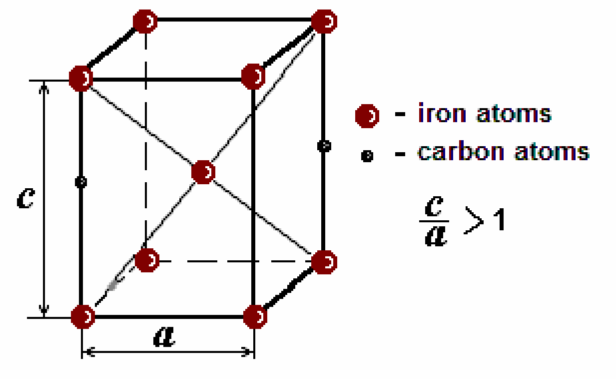


Figure 10.10 Unit cell of martensite

As a result of diffusionless transformation FCC crystalline lattice of austenite is reconstructed to the BCC structure. But as in this lattice all the carbon atoms remain (in this case 0.8 % wt.) in each unit cell of α iron, this cell is deformed, extended and from cubic shape becomes tetragonal (Fig. 10.10). A measure of distortion of iron lattice is the relation of height of unit cell *c* to the basis side length *a*. The relation *c*/*a* increases with the increase of carbon content in solid solution.

The martensitic crystal has the shape of the plate similar to a convex lens. In cross-section of metallographic specimen it usually looks like a needle. The first martensite crystal arisen in austenite grain is limited by the sizes of this grain; crystals forming further do not cross each other and do not pass through the grain boundaries of austenite, therefore they have smaller sizes (Fig. 10.11). It is obvious that martensitic transformation, as well as pearlitic one, refine the grain of steel. Needle-shaped grains of martensite may be observed in Figure 10.13.

Of the various microstructures that may be produced for the given steels, martensite is the hardest and strongest and, in addition, the most brittle; it has, in fact, negligible ductility. Its hardness is dependent on the composition: the more carbon content, the harder martensite. For example, for carbon content of 0.8 % wt. hardness of martensite makes 65 *HRC* (670 *HB*); on the contrary, percent elongation and impact strength are close to zero. Martensite is a brittle structure; it cannot be plastically deformed or processed by cutting tool, except for abrasive one.

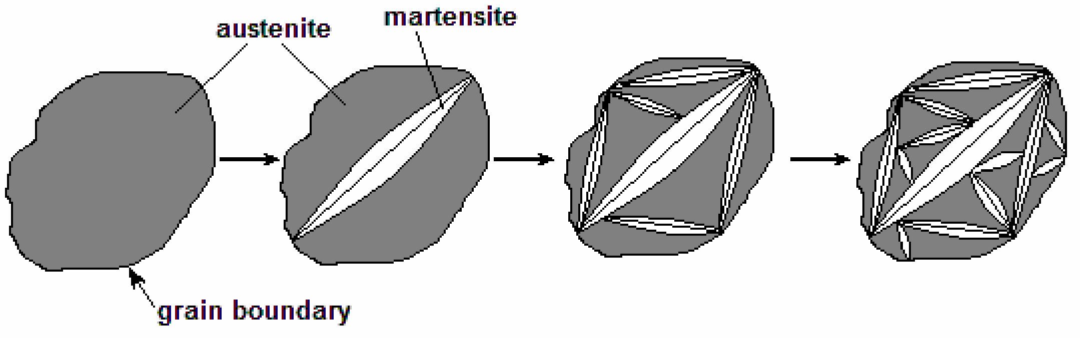


Figure 10.11 Scheme of martensite formation

High hardness of martensite is a result of stengthening caused by simultaneous action of all mechanisms of restricting the dislocations motion:

1) solid solution strengthening by dissolved atoms of carbon;
2) strain hardening caused by the growth of martensitic crystals;
3) strengthening by the grain size reduction;
4) strengthening by disperse particles of cementite Fe_3C.

The main contribution to hardening is given by distortions of α iron crystal lattice by the interstitial atoms of carbon. Therefore hardness of martensite depends on carbon content (Table 10.2).

Table 10.2 Hardness of martensite depending on carbon content

Content of carbon in martensite, % wt.	0.2	0.3	0.4	0.5	0.6	0.8	1.0
Hardness, *HRC*	40	48	55	59	62	65	66

The martensite grains grow at a very high rate equal to the velocity of sound within the austenite matrix (≈5 km/s). Sometimes there is a sound effect produced. Prominent feature of martensitic transformations: it develops only at continuous cooling to a point M_f. At increase in the carbon content temperatures of points M_s and M_f go down, and martensitic transformation is displaced in the field of lower temperatures (Fig. 10.12).

It means that in actual practice of thermal processing all martensitic interval is not passed: usually cooling is carried out to the indoor temperature, i. e. approximately not lower than 20 °C. Therefore martensitic transformation in steels containing more than 0.6 % wt. C does not reach the end, and after quenching the steel structure comprises some quantity of austenite. It is called *retained austenite*.

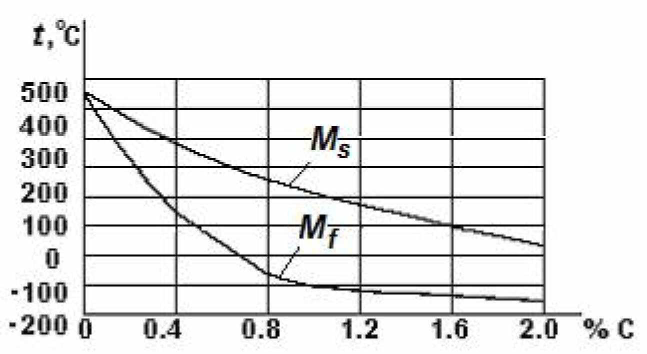


Figure 10.12 Dependence of temperatures of the beginning and the termination of martensitic transformation on the carbon content in steel

The quantity of retained austenite in the steel after quenching depends on the carbon content and temperature of the cooling medium. It can make some percent in high-carbon steels and tens percent in the alloyed steels.

To reduce the amount of retained austenite in high-carbon tool steels, they undergo cold treatment.

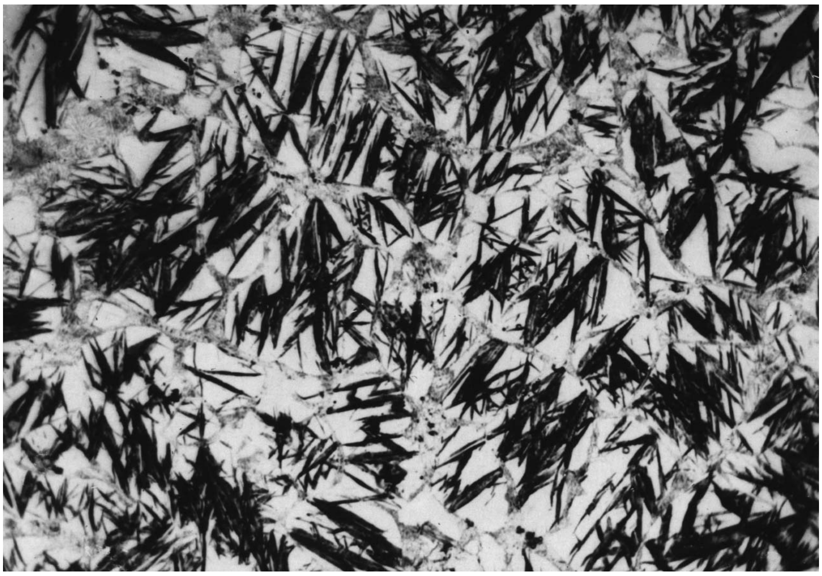


Figure 10.13 Photomicrograph of martensitic microstructure. The needle-shaped grains are the martensite phase, and the white regions are austenite that failed to transform during the rapid quenching. ×600

10.6. TRANSFORMATION UPON HEATING OF MARTENSITE

Martensite is a nonequilibrium single-phase structure; however, steels retain their martensitic structure at room temperature.

The atoms of carbon introduced in a crystal lattice of α iron, create internal stresses. Each carbon atom is a point defect. Besides, in martensite the dislocation density (10^9-10^{12} cm^{-2}) is great. Therefore martensite possesses the raised storage of internal energy. At a room temperature it can remain unrestrictedly long, but as soon as heating will give to atoms of carbon the additional energy necessary for diffusion, transformation of martensite to more equilibrium phases will begin.

At martensite heating carbon is precipitated out of α solid solution, forming thus cementite Fe_3C. Martensite dissolves onto ferrite and cementite mix. Depending on temperature and time of transformation there can appear spheroid structures – temper sorbite or troostite – instead of lamellar structures, received at transformation of overcooled austenite (Fig. 10.14).

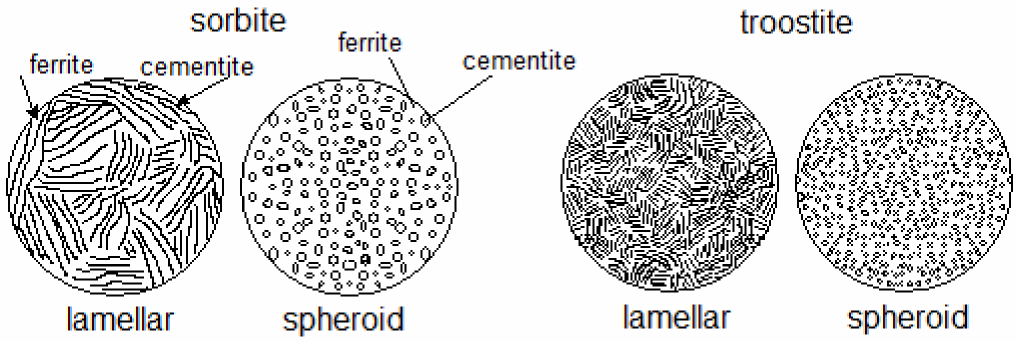


Figure 10.14 Microstructure of lamellar and spheroid ferrite and cementite mixes having different grain size

So, under heating of martensite there are following processes:

1) decrease of carbon content in martensite and cementite formation;
2) reduction of internal stresses;
3) growth of cementite particles;
4) transformation of retained austenite to martensite (it is important for steels with the carbon content > 0.6 % wt. and especially for alloyed steels).

10.7. HEAT TREATMENT OPERATIONS

Annealing

The term ***annealing*** refers to a heat treatment in which a steel is exposed to an elevated temperature for an extend time period and then slowly cooled usually staying inside the furnace. Ordinarily, annealing is carried out to (1) relieve stresses; (2) increase softness, ductility and toughness; and/or (3) produce a specific microstructure.

Figure 10.14 shows the portion of the iron–carbon phase diagram. The horizontal line at the eutectoid temperature, labeled A_1, is termed the *lower* *critical temperature*, below which all austenite will be transformed into ferrite and cementite phases. The phase boundaries denoted as A_3 and A_{cm} represent the *upper critical temperature* lines, for hypoeutectoid and hypereutectoid steels, respectively. Above these boundaries, only the austenite phase will exist.

A heat treatment known as *full annealing* is often utilized in low- and medium-carbon steels in order to increase their ductility before plastic deformation. The alloy is heated to 15 or 40 ºC above the A_3 or A_1 lines as indicated in Figure 10.14. The alloy is than furnace cooled; that is, the heat-treating furnace is turned off and both furnace and steel cool to room temperature at the same rate, which takes several hours. The microstructural product of this heat treatment is coarse pearlite that is relatively soft and ductile.

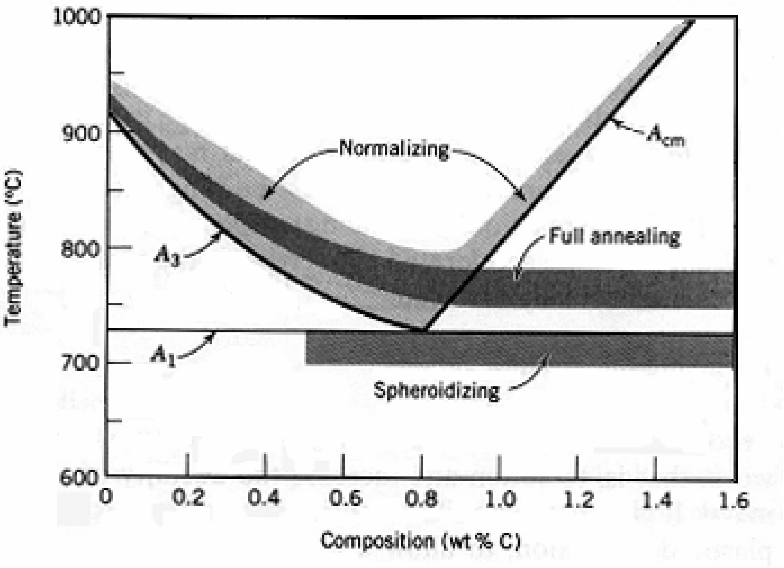


Figure 10.14 The iron–iron carbide phase diagram, indicating heat treating temperature ranges for plain carbon steels

An annealing heat treatment called normalizing is used to refine the grains (i. e., to decrease the average grain size) and produce a more uniform size distribution. Fine-grained steels are tougher than coarse-grained ones. *Normalization* is heating at approximately 55 to 85 ºC above the upper critical temperature followed by cooling in air.

High-carbon steels having a microstructure containing even coarse pearlite may still be too hard. These steels may be heat treated to develop the spheroidite structure. Spheroidized steels have a maximum softness and ductility and are easily deformed.

The *spheroidizing* heat treatment consists of heating the alloy at a temperature just below the eutectoid in the α + Fe_3C region of the phase diagram. The time required ordinarily ranges between 15 and 25 h. During this annealing there is a coalescence of the cementite to form the spheroid particles (Fig. 10.15).

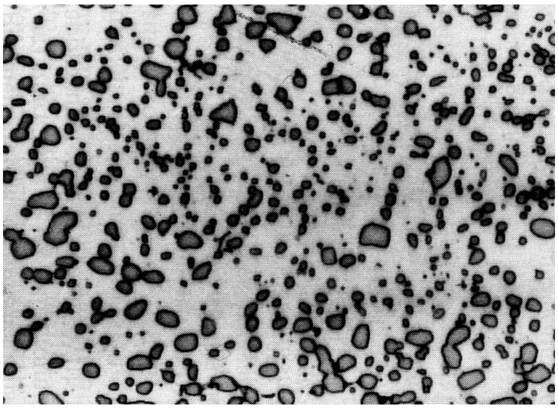


Figure 10.15 Photomicrograph of a steel having a spheroid microstructure. The small particles are cementite; the continuous phase is α ferrite. ×1000

Quenching

Conventional heat treatment procedures for steels performing in order to increase their hardness involve continuous and rapid cooling of an austenitized specimen in some type of quenching medium, such as water, oil, or air. During the quenching treatment the optimum properties of steel can be realized only if the specimen has been converted to martensite, without formation of any pearlite. Thus, the quenching rate must be greater than the critical one.

Quenching is a strengthening heat treatment, which changes steel structure so that to raise hardness and strength as much as possible.

Quenching consists in heating the steel above temperature of phase transformation with subsequent fast enough cooling (cooling rate should exceed the critical one).

<u>The purpose</u> is to obtain the non-equilibrium structure: a supersaturated solid solution of carbon in α iron, called martensite. The practical purpose is obtaining the maximum hardness, possible for the given steel grade.

Rapid cooling upon quenching is necessary, so that carbon has no time to precipitate from the solid solution – austenite – and remains in a lattice of iron after cooling.

For quenching treatment of steel, it is necessary to choose

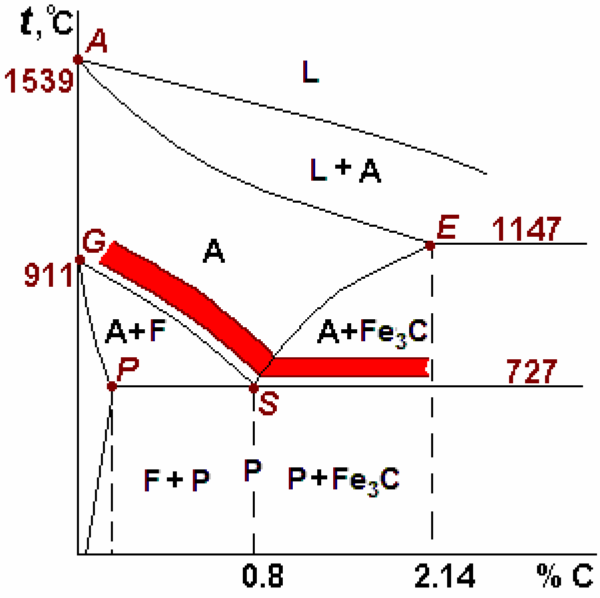


Figure 10.16 Temperature range of heating steel for quenching

heat temperature and cooling rate correctly. These two parameters define the result of quenching.

To select the right temperature of quenching, the following rule is appriciable: a hypoeutectoid steel must be heated to 30-50 ° above critical point Ac_3, and hypereutectoid steel – to 30-50 ° above point Ac_1 (Fig. 10.16). Small excess of a critical point is necessary, as some temperature variations about a preset value are inevitable in heating furnaces.

Why the temperature is chosen being different for either hypoeutectoid or hypereutectoid steel?

Structure of a hypoeutectoid steel below line *GS* includes ferrite. If steel is quenched from this temperature field, the austenite will turn to a hard and strong martensite, and ferrite will not change since it is an equilibrium phase. As soon as ferrite is very soft material, therefore, the presence of ferrite grains in quenched steel structure reduces its hardness. Thus, the purpose of quenching will not be attained. Therefore it is necessary to heat steel up to higher temperatures (above line *GS*), where ferrite is already missing.

Quenching from single-phase (austenitic) field, i. e. from temperatures above Ac_3, is called *a full hardening*. It is intended for hypoeutectoid (constructional) steels.

For hypereutectoid steels such a high temperature heating is not required, because their structure consists of austenite and cementite above point A_1, but below the line *SE*. Upon quenching from this field austenite will turn to martensite, and cementite will be retained, as an equilibrium phase. Presence of such hard structural component in cooled steel is useful because small particles of cementite are additional obstacles for dislocation motion; they raise hardness and wear resistance.

Quenching from two-phase fields, where austenite and cementite, or austenite and ferrite are present, is called *an underhardening*. It is applied for hypereutectoid (tool) steels.

Critical cooling rate during quenching of carbon steels is not lower 400 °C/s. Such a value is attained upon cooling in water or water solutions of salts (NaCl) and alkalis (NaOH), increasing cooling capacity of water. While quenching, it is necessary to move the work-piece vigorously in a cooling liquid to reduce steaming from a metal surface because it retards the cooling. Critical cooling rate of alloying steel is much lower therefore it is possible to apply softer hardening mediums – mineral oils or solutes of polymers.

Four quenching methods are distinguished.

1) *Continuous quenching (quenching in one hardening medium)* (see Fig. 10.17, curve 1). It is the simplest way but may result in generation of high internal stresses inside the work-piece.

2) *Quenching in two hardening mediums*, or *broken quenching* (Fig. 10.17, curve 2). Following this way the steel is quickly cooled in the range of temperatures 750-400 °C, and then a work-piece is carried to another hardening medium, whose cooling capacity is lower. So, in martensitic temperature range cooling occurs slowly. It leads both to lower internal stresses and reduced probability of crack formation. An example of such a method is a process of cooling a piece at first in water, and then in oil.

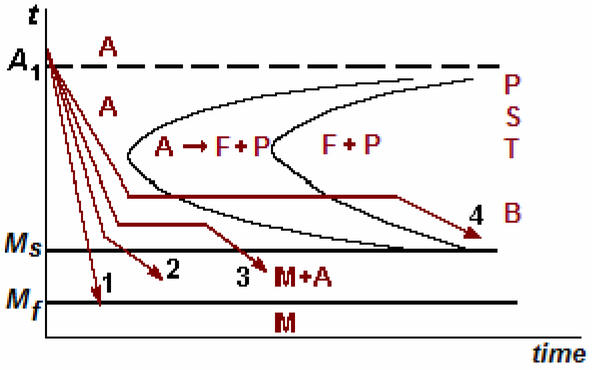


Figure 10.17 Modifications of quenching by the way of cooling

3) *Graduated quenching* (Fig. 10.17, curve 3). The heated work-piece is drawn into the liquid medium with temperature on 20-30° above point M_s. Fast cooling of steel in the top range of temperatures is thus provided, and then the holding is carried while the temperature is levelled in a work-peace cross-section, so, thermal stresses decrease. Then this work-peace is taken out from a quenching bath, and the further cooling occurs in other medium, more often either in air or oil. In this case martensitic transformation occurs at slow cooling that leads to lower internal stresses. Liquid mediums for graduated quenching are melted alkalis, saltpeter and fusible metals.

4) *Isothermal quenching*, or *bainitic* hardening (Fig. 10.17, curve 4). It essentially differs from other ways. The holding in the cooling medium at the temperature of bainitic transformation proceeds until full decomposition of austenite. In all previous cases quenching produced martensite structure, and in this case it gives bainite.

Upon isothermal quenching the stresses in steel are minimum, formation of cracks is excluded, deformation is low. For some alloyed steels (spring and die steels) this way of quenching allows to receive an optimum combination of strength and plasticity.

So, graduated and broken quenching reduces hardening stresses as the difference of temperatures between the piece centre and its surface decreases. But because of very small period of overcooled austenite existence in plain carbon steels these methods are applied for the alloyed steels more often.

Possible ***defects of quenching***:

a) *overheating* gives coarse grains;

b) *overburning* is an oxidation of grain boundaries and gives extremely coarse grain;

c) *underheating* is a quenching of hypoeutectoid steels from temperature range Ac_1–Ac_3. It leads to duplex structure (martensite + ferrite) and low mechanical properties;

d) *distorting* and *cracks* are caused by internal stresses. Specific martensite volume is higher that of austenite and therefore internal stresses are in steel structure. Especially they are dangerous for parts of the difficult shape and when the structural stresses add to thermal ones, arisen due to a temperature difference between surface and centre.

To avoid distorting, thin items such as for example saws, hacksaw blades, razors should be cooled in special quenching presses.

Two important notions are closely connected with technology of quenching.

Hardenability is an ability to receive high hardness upon quenching. Hardenability depends on the carbon content in steel and is characterised by the maximum possible hardness (*HRC*) for the given steel grade.

Hardness penetration is steel ability to receive the hardened layer of certain depth. Rate of cooling decreases as a distance from sample's surface to the centre, therefore it can happen for the thick enough samples the cooling rate will be lower than critical one in the sample's core (Fig. 10.18). In this case only surface layer will receive hardening and acquire the martensite structure whereas the core will stay not-quechned and composed of soft ferrite and pearlite structures.

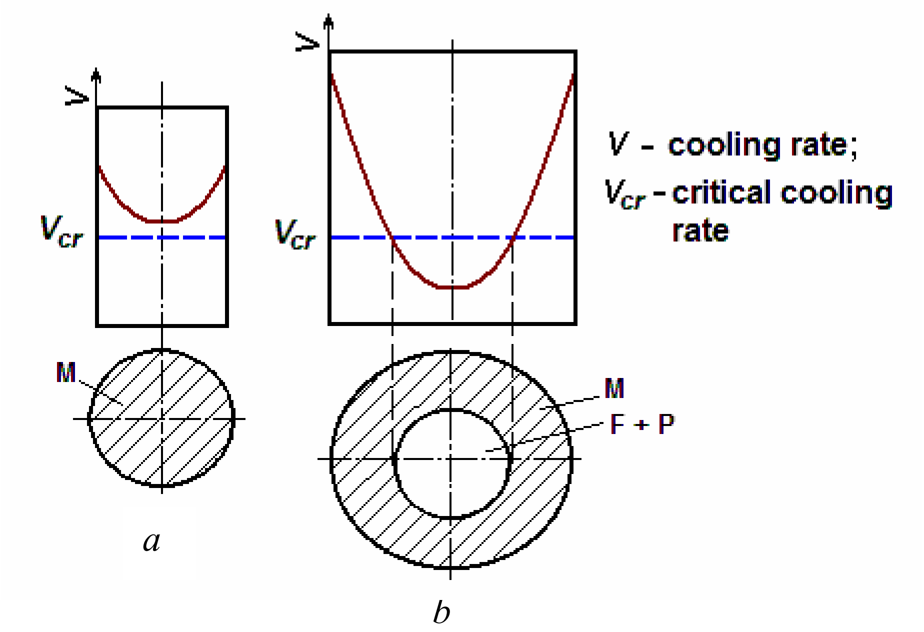


Figure 10.18 Alteration of cooling rate in cross-section of a part:
a – of small diameter; *b* – of big diameter

The characteristic of hardness penetration is a value of critical diameter. *Critical diameter* is the maximum diameter of cylindrical bar which is quenched through in the particular cooling medium.

The deeper is the hardness penetration in a steel, the better it is for steel. Carbon steels have critical diameter 10-15 mm only if being cooled in water. The hardness penetration depends on the amount of alloying elements which complicate diffusion decomposition of austenite, thereby reducing the critical speed of cooling upon quenching. The more alloying elements are there in steel, the higher is the hardness penetration.

Tempering

Being extremely brittle martensite cannot be used for most applications, but its ductility and toughness may be enhanced by heating to temperatures at which diffusion rate becomes appreciable. Upon heating to temperatures below the eutectoid, martensite transforms to the equilibrium ferrite and cementite phases.

Tempering heat treatment is performed to produce more stable and ductile structure other than martensite. Normally, tempering is carried out at temperatures between 250 and 650 ºC. The microstructure of tempered martensite consists of extremely small cementite particles embedded within a continuous ferrite matrix.

Tempering is carried out by heating the steel up to temperatures below critical ones with the subsequent cooling usually in air.

The purpose of tempering is to form a required complex of steel service properties, obtain more stable steel structure in comparison with quenched one, and reduce internal stresses.

Tempering is the last operation in a technological process of steel heat treatment, therefore the structure formed upon tempering should provide the properties necessary for service.

In the course of tempering there occurs decomposition of martensite at the expense of carbon precipitation from the martensite. The higher is the temperature and longer is the holding time, the more carbon is precipitating out of the solid solution. Both the internal stresses and dislocation density therefore reduce. Upon heating carbon is precipitating from retained austenite, too, therefore the temperature of point M_s raises. Low-carbon austenite transforms to martensite which then decomposes onto ferrite and cementite mixture.

By the temperature of heating, the tempering is subdivided into 3 types: low, medium and high.

Upon *low-temperature* (or *low*) *tempering* (150-200 °C) a part of excess carbon precipitates from martensite forming the smallest carbide particles. But as the diffusion rate is still low, some amount of carbon still remains in the solid solution. Thus, such a structure is composed of low-carbon martensite and very fine carbide particles. It is called *tempered martensite*.

As a result of low tempering internal stresses reduce, both toughness and plasticity grow moderately and hardness almost does not drop. Thus treated pieces can work under conditions where high hardness and wear resistance are required.

Low tempering is applied for treating the cutting and measuring tools, as well as for parts of rolling bearings.

Medium-temperature (or *medium*) *tempering* is carried out at higher temperatures: 300-450 °C. Thus all excess carbon leaves α-Fe lattice with formation of cementite particles. Tetragonal distortions of an iron crystal lattice disappear, it becomes cubic again. Martensite transforms to the ferrite and cementite mixture with very small needle-shaped particles of cementite. This structure is called *tempered troostite*.

Medium tempering serves to further reduce the internal stresses, improve toughness. Thus strength remains high enough and both yield strength and fatigue limit reach their maximums. This type of tempering is applied for elastic elements like springs, spring plates and also for die tools.

In the range of 500-650 °C, diffusion rate is high enough to provide decomposition of martensite into ferrite and cementite with large spherical carbide grains. Such a treatment is called *high-temperature* (or *high*) *tempering*; the resulting structure is *tempered sorbite*.

As a result of high tempering, both toughness and plasticity of steel strongly increase, internal stresses are relieved almost completely, hardness and strength decrease, but nevertheless remain high enough.

High-temperature tempering is applied for parts of machines subjected to complex loading: static, dynamic and alternating ones. High tempering provides the best combination of strength, plasticity and impact toughness.

Quenching combined with high tempering is called *a heat refining*, or *a toughening*. The special group of structural steels with the contents of carbon from 0.3 to 0.5 % wt. is exposed to such kind of processing. They are called *heat-hardenable steels*. After such a heat treatment steel has higher characteristics of strength (TS and σ_y), plasticity (δ and ψ) and toughness (KCU) in comparison with steel after annealing.

Change of carbon steel mechanical characteristics upon tempering is shown in Figure 10.19.

So, the ductility of steels improves both with the temperature and duration of tempering, but in the same time its hardness and durability decrease. In practice of thermal processing a mode of tempering is chosen according to properties required by service conditions.

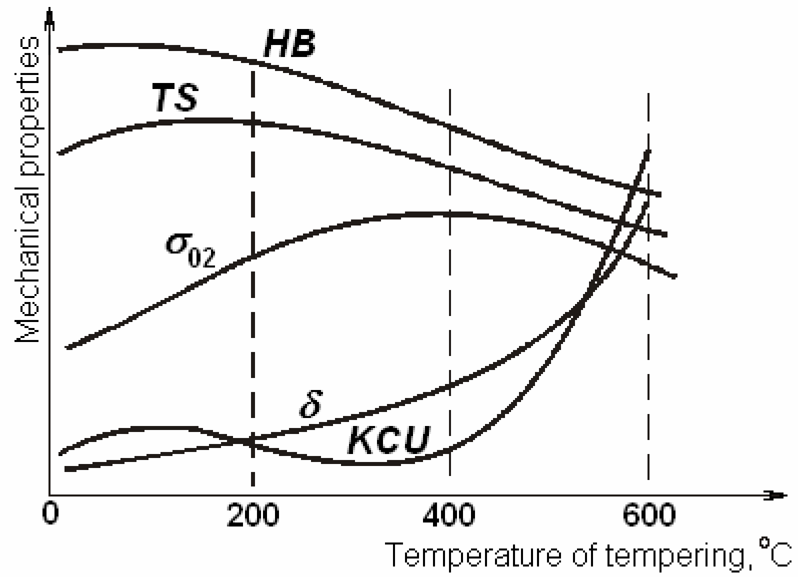


Figure 10.19 Tempering temperature influence
on mechanical properties of the quenched carbon steel

Surface hardening

For some parts of machines high surface hardness and wear resistance should combine with high fracture toughness of a core metal. It concerns the parts which experience the wearing with simultaneous action of dynamic loadings (for example, gear wheels, king bolts fastening track links of tracklaying vehicles).

In such cases only thin enough surface layer may be subject to hardening instead of the whole component.

Surface hardening is carried out by heating the surface layer of the sample to temperature range of quenching and following fast cooling which results in creating the martensite structure within this layer only.

Quenching is carried out by fast heating of the surface layer whereas the core stays almost at the same temperature at the expense of finite heat conductivity. Upon such short-time heating the temperature in the cross-section of a sample falls sharply from a surface to the centre.

After cooling, three typical zones with different structure and properties (see Fig. 10.20) are found below the surface.

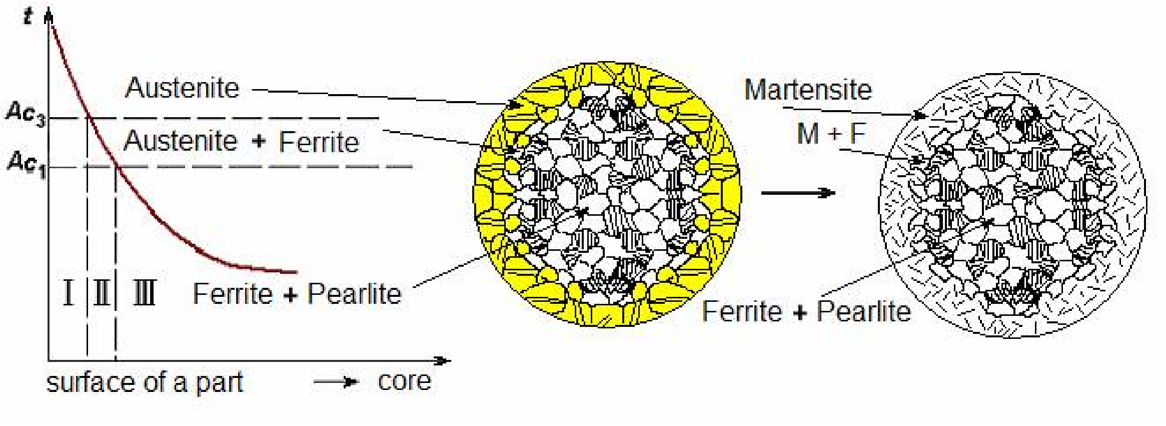
In a zone I after quenching the martensite structure with the maximum hardness appears since this zone was heated up above critical temperature Ac_3.

In a structure of zone II after quenching, except martensite, there is ferrite. Hence, the hardness numbers will be lower.

In a zone III heating and cooling do not lead to any changes of structure. It means that initial ferrite and pearlite structure with low hardness, but high plastic properties is retained here.

After surface hardening the work-piece can resist dynamic loadings at the expense of a tough core and work well under the wear conditions due to hard surface.

The fast heating of a surface necessary for such technology, is carried out more often by the magnetic induction method. The work-piece is placed into inductor connected to the generator of a high frequency current. The alternating magnetic field of high frequency induces eddy currents in a thin surface layer of metal, and heating is carried out at the expense of metal resistance to these currents. Immediately after heating which lasts seconds, a piece is placed into sprayer for cooling.



a *b* *c*

Figure 10.20 Surface hardening of steel:
a – temperature distribution across section; *b* – structure under surface heating;
c – structure after quenching

Surface hardening should be accompanied by low tempering.

The higher is the frequency of an external alternating magnetic field, the thinner is a layer in which eddy currents are concentrated. Therefore depth of the hardened layer can easily be regulated and makes from the tenths of millimetre to 3-5 mm. Operation of high frequency quenching can be automated completely. The method is very productive; distorting and oxidation of a part surface is thus minimal.

Steels of lowered hardness penetration were worked out specially for such way of heat treatment. They contain about 0.55 % wt. of carbon and less than 0.5 % wt. of impurities.

Chemical heat treatment

Chemical heat treatment of steel is a diffusion saturation of steel surface with various elements on purpose to strengthen a surface and to protect metal against corrosion.

There are many kinds of chemical heat treatment, but in any case it is necessary to provide a saturating atmosphere with high concentration of atomized active element. Atoms or ions are adsorbed by a metal surface, and then at the expense of diffusion get deep into. It results in formation of diffusion layer different from the base metal both by chemical composition, structure and properties.

Questions and problems

1. What is heat treatment?
2. Explain what phase transformations appear in steel while heated above the critical points Ac_1, Ac_3, Ac_{cm}.
3. Analyze phase transformations upon heating of hypoeutectoid steel.
4. Analyze phase transformations upon heating of hypereutectoid steel.
5. Why the grain size is a major criterion of steel heat treatment quality?
6. Why grain refining occurs upon steel heating?
7. Analyze the diagram of isothermal austenite transformation for steel with 0.8 % wt. C. What do all the lines mean on the diagram?
8. Characterize three types of supercooled austenite transformation.
9. Describe the *equilibrium (pearlitic) transformation*: its mechanism, conditions, and products.
10. Describe the *nonequilibrium (martensitic) transformation*: its mechanism, conditions, and product.
11. Give the definition to *martensite.* Characterize its structure and properties?
12. Why martensite is nonequilibrium structure?
13. What happens with martensite when it is heated? What structures are formed as a result of martensite decomposition?
14. What is *annealing*? Purpose and kinds of annealing.
15. What is *normalizing*? Purpose and structure.
16. Steel *quenching*: purpose and technique.
17. What methods of quenching exist in dependence on heat temperature and way of cooling?
18. List quenching defects. What are overheat and overburning?
19. By what method a surface hardening can be obtained?
20. What is *hardenability* and *hardness penetration* upon steel quenching?
21. What is *tempering*? Purpose and kinds of tempering.
22. Give the notion of *chemical heat treatment*. What is the purpose and kinds of this treatment?

11. NONFERROUS METALS AND ALLOYS

Application of metals by the humans beings began with nonferrous metals. In the beginning they were native metals: copper, gold, silver, then tin and lead.

Characteristic features of nonferrous metals are:

- colour,
- high ductility,
- low hardness,
- low melting temperature,
- absence of polymorphic transformations.

A conventional classification of nonferrous metals includes following groups:

Noble	Light	Low-melting	Refractory
Pt, Ag, Au, [Cu]	Be, Mg, Al, [Ti]	Zn, Sn, Pb, Sb, Bi, Hg	W, Mo, Ta, Nb

11.1. ALUMINUM ALLOYS

Aluminum is a light weight metal: $\gamma = 2{,}7 g/cm^3$. $t_m = 660$ °C. Aluminum possesses important advantages: the low density, high electro-conductivity, the big unit strength. For example, the aluminium alloy has strength $\sigma_T = 700$ MPa and unit strength $\sigma_T/\gamma = 23$. (For steels this characteristic does not exceed 15.)

By production yield aluminum and its alloys are at second place in the world after iron.

Useful properties of *commercial aluminum* are applied in following areas:

1) high plasticity is used for thin foils production (packing, armature of condensers, decorative application);

2) high electro-conductivity (65 % from copper conductivity) is demanded in the electrical engineering (electric main, cores of cables);

3) high corrosion resistances (a film of oxide Al_2O_3 10 μm in thickness protects a metal surface) is necessary for home appliances, for storage of a foodstuff, vessels for aggressive liquids;

4) high reflective ability is important for manufacturing of projectors, reflectors, TV screens;

5) high heat conductivity allows manufacturing of heat exchangers in refrigerators.

Examples of products made of commercial aluminum: pipelines, deck superstructures of ships, wires, cables, bus bars, frames, racks, consoles, office furniture, tanks (dairy, etc.).

Aluminum forms chemical compounds and limited solid solutions with the majority of alloying elements.

Aluminum alloys are subdivided into *cast* and *wrought alloys*, and also into *strengthened* and *not strengthened* by thermal processing. The generalized state diagram aluminum – an alloying element (fig. 11.1) allows subdivide alloys as follows:

W – wrought alloys,
C – cast alloys,
NS – alloys not strengthened by heat treatment,
S – alloys strengthened by heat treatment.

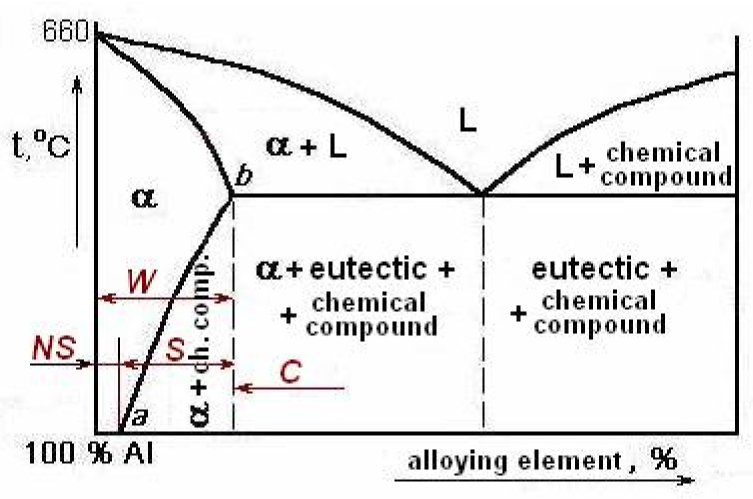


Figure 11.1 State diagram aluminum – alloying element

Wrought aluminum alloys not strengthened by thermal processing

These are alloys with magnesium and manganese. Grades are designated АМг and АМц (in Russia). The alloys are applied to the products manufactured by a deep drawing and welding. Welding is carried out by nonconsumable tungsten electrode in argon; another ways are a resistance welding or friction stir welding. Alloys are rather plastic and corrosion-resistant. They are strengthened by cold-working. Al–Mg and Al–Mn alloys are capable to structural hardening (press effect is appear as precipitating of small intermetallic particles while processing by pressure).

Examples of products: welded vessels, pipelines of gasoline and oil, frames, automobile bodies, ship hulls and masts.

Wrought aluminum alloys strengthened by thermal processing

First of all, these are the most widespread aluminum alloys – *duralumins*. The word “duralumin” (French term) means “hard aluminum”. Duralumins are designated by the letter “Д” and a grade serial number.

Besides, this group includes wrought aluminum alloys (designation АК), avial (АВ), high-strength aluminum alloys (В)[1].

Grades of duralumins (in Russia): Д1 – normal, Д16 – “superduralumin”, Д18 – rivet alloy. All of them contain copper (about 4 % wt.), magnesium and manganese.

Copper is the main alloying element in duralumins, therefore it is possible to study phase transformations in alloys using the Cu–Al state diagram (Fig. 11.2).

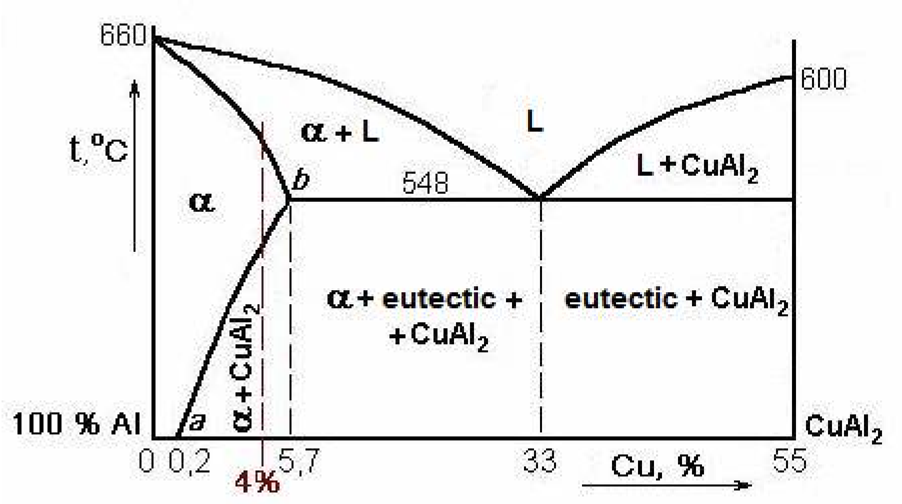


Figure 11.2 State diagram aluminum – copper

Phases, equilibrium under the room temperature are the follows: α is a solid solution of copper in aluminum, $CuAl_2$ is a chemical compound or intermetallic phase (Fig. 11.3). The eutectic consists of these two phases: E = α + $CuAl_2$.

Line *ab* is a line of limited solubility of copper in a crystal lattice of aluminum. Alloys found under this curve 0.2 to 5.7 % wt. Cu can be strengthened by heat treatment: quenching and ageing. However, the mechanism of strengthening here is different than that of martensite tempered steels.

In annealed alloy particles of $CuAl_2$ are rather large; the alloy is soft and ductile (see Fig. 11.4, *a*).

Upon heating for quenching (above the line *ab*) particles $CuAl_2$ are dissolved, atoms of copper and other alloying elements form a substitutional solid solution in the aluminum lattice.

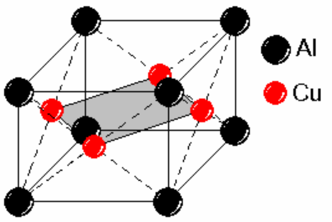
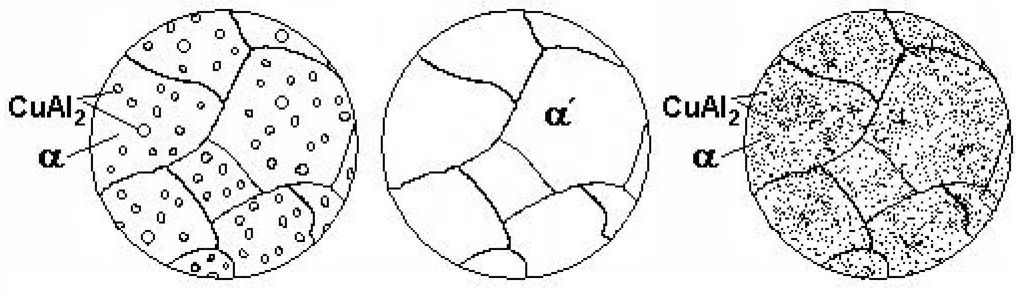


Figure 11.3 Crystal lattice of intremetallic phase $CuAl_2$

---

[1] Russian letters

Upon the fast cooling in cold water the diffusion is suppressed and at the room temperature, the solid solution is retained, and becomes supersaturated (α′), as shown in Figure 11.4, *b*. Its hardness and strength are not high; they exceed the values for annealed alloy by 25 % only since it is a substitutional solid solution.



a *b* *c*

Figure 11.4 Microstructure of duralumin:
a – after annealing; *b* – after quenching; *c* – after ageing

Eventually at the room temperature *a natural ageing* is started and supersaturated solid solution sites enriched by copper precipitate. Around them, the crystal lattice becomes strained and this serves to retard the moving dislocations (Fig. 11.4, *c*). The alloy becomes stronger. Natural ageing usually takes 5 through 7 days.

When heated the ageing process occurs at higher rate. It is so-colled *artificial ageing*. The higher is the temperature of artificial ageing, the faster is the decomposition of solid solution. $CuAl_2$ particles precipitate from the copper-enriched zones and grow then with temperature and holding time. Therefore distance between them increases, and the effect of hardening decreases, as $\Delta\sigma_T \sim \frac{1}{R}$, where R is a distance between particles.

The same processes occur in other alloys based on aluminum. But the structure and composition of intermetallic phases are different.

So, strengthening heat treatment of duralumin consists in quenching from 500-510 °C and natural ageing for 5-7 days or artificial ageing (for the alloys that serve at the raised temperature).

As a result of quenching and natural ageing, the Д16 duralumin acquires strength σ_T = 540 MPa, that exceeds tensile strength of some steels of ordinary quality.

Alloy named *avial* is less strong, than duralumin, but more plastic (it contains ≤0.5 % wt. Cu and Si).

Wrought aluminum alloys contain the same components, as duralumin, and, in addition, silicon. Parts are manufactured by forging or stamping at

450-475 °C, followed by quenching and artificial ageing. Alloys are applied for producing parts of the complex shape.

Thermally treated high-strength aluminum alloys have σ_T = 600-700 MPa; the yield strength is almost equal to tensile strength. These are alloys of system Al – Zn – Mg – Cu, sometimes with addition of Cr or Zr. To increase their corrosion resistance sheets are plated with pure aluminum added with 1 % Zn.

All aluminum alloys of this group are intended for aircraft. Many airplane parts are made of them: blades of screws, frames, draughts of management, a covering of planes, stringers, longerons.

Cast aluminum alloys

Cast alloys contain silicon, copper or magnesium.

Silumin is an alloy based on aluminum alloyed with silicon. It has the best foundry properties. For refining of grain an alloy is modified with sodium (a mix of salts NaCl + NaF).

Some foundry alloys can be strengthened by thermal processing. For different kinds of casting alloys are designed specially (for example, alloys for casting under pressure).

This group of aluminum alloys is applied, basically, for difficult thin-walled castings: parts of automobile engines (crankcases and blocks of cylinders, cases of compressors).

Heat resisting aluminum alloys

They are able to work at temperatures up to 300 °C (pistons, impellers, parts of turbojets compressors, a covering of supersonic planes).

The alloys have complicated composition: they contain iron, nickel, titanium, zirconium. They can be both wrought and foundry.

Some alloys have their recrystallization temperatures above deformation and quenching temperatures, i. e. polygonized structure remains after deformation and heat treatment. It gives structural hardening on 30-40 % more in comparison with alloys that were recrystallized.

Annually in the world there is produced about 20 million t of aluminum. In Russia aluminum is produced at Krasnoyarsk, Volgograd, Irkutsk and other aluminum factories. In December, 2006 in Abakan (Khakassia) the aluminum factory with capacity of 300 thousand tons a year had been put in operation. It is the first of a kind enterprise for the last 20 years.

11.2. TITANIUM ALLOYS

It is difficult to classify titanium to any one group of nonferrous metals. It is refractory (t_m = 1669 °C), at the same time it is possible to regard it as light metal (γ = 4.5 g/cm^3). Without being noble metal, it perfectly resists corrosion in various environments. As well as iron, titanium has polymorphic transformation: Ti_{α} with HCP lattice at 882 °C turns to Ti_{β} with BCC lattice.

Titanium is widespread in the earth crust: it takes the fourth place after aluminum, iron and magnesium. But industrial application of this unique metal began only in 1950th, basically, for military purposes. It is explained by complexity of extraction of the titanium from ores, multistage process of clearing that leads to rather high prices for metal (approximately 90 times more expensive than iron).

Advantages of the titanium are:

- low density,
- very high unit strength (σ_T = 1300-1600 MPa and unit strength $\sigma_T / \gamma \geq 30$),
- the highest corrosion resistance (except for the concentrated sulfuric, nitric and fluoric acids),
- high impact strength even at negative temperatures (KCU = 1-1.6 MJ/m^2 at temperature of liquid hydrogen –253 °C),
- ability of alloys to be strengthened by heat treatment.

Lacks of the titanium, as constructional material:

- high cost (poor ores, difficult metallurgical treartment),
- active interaction with gases while heating,
- low value of the module of elasticity E (approximately 2 times less, than for iron),
- bad machinability in comparison to steels.

Nevertheless, processes for manufacturing the articles from titanium alloys by casting, processing by pressure, welding and cutting develops continuously and improves.

The basic alloying elements in titanium alloys are Al, V, Mo, Cr, Zr, Mn. Aluminum in titanium alloys plays the same important role, as carbon in steel. Alloying elements can stabilize either low-temperature α phase or the high-temperature phase β. Solubility of components in titanium depends on the temperature; therefore, strengthening heat treatment is possible. For different alloys it includes quenching and tempering, or quenching and ageing.

Upon slow cooling transformation $Ti_{\alpha} \rightarrow Ti_{\beta}$ occurs at the expense of the diffusion by nucleation a new phase centers and their growth. Upon fast cooling a shear mechanism develops similar to martensite transformation in steels. The structure is called martensite, too, and has needle structure. However, titanium martensite does not possess the high hardness and strength of martensite formed in steel. It is ductile enough. The matter is that the nature of solid solutions is different: carbon forms with iron an interstitial solution, and aluminum with the titanium – substitutional one.

It is also possible to preserve overcooled β phase at a room temperature (similarly austenite in steels). In some alloys eutectoid is formed, but it is brittle and does not improve mechanical properties of an alloy.

Fields of application of titanium alloys:

1) aircraft and rocket production (a covering of supersonic planes, cases of engines, cylinders for gases, nozzles, disks and blades of the aviation engine compressor, parts of fuselage, fixture, cases of the second and third steps of rockets);

2) chemical industry (compressors, valves, gates, cylinders for liquid gases and aggressive liquids);

3) shipbuilding (rowing screws, a covering of sea-crafts and submarines);

4) equipment for processing of nuclear fuel;

5) cryogenic techniques (working at very low temperatures).

11.3. COPPER ALLOYS

Copper is a heavy metal ($\gamma = 8.9$ g/cm^3) with FCC lattice; it does not have any polymorphic transformations. Temperature of fusion is 1083 °C. It is possible to call copper “the most colourful” metal: its surface is red, and a fracture is pink.

Pure copper is applied more often in the electrical engineering and electronics. Copper possesses high electrical conductivity therefore it is used as a current conductor (buses, cable cores, windings of electric motors, contacts).

The highest heat conductivity of copper allows making water cooled crucibles, crystallizers, pallets, ingot moulds etc.

Copper shows corrosion resistance in atmosphere, sea, river and tap water, in other excited environments.

Technological properties of copper are not so good: it is very ductile and can be easily processed by pressure, but it has bad machinability. Foundry properties are low (copper gives notable shrinkage); copper is hard to weld, but easy to solder.

Copper has low strength: from 160 MPa in a cast condition to 240 after hot deformation. Nevertheless, the wire drawn is cold worked up to σ_T = 450 MPa.

Copper is supplied in the form of rolled shapes: sheets, bars, pipes and wire.

Copper alloys represent solid solutions based on copper. They are both stronger and more plastic than pure copper. Strength of copper alloys is equal to strength of annealed low-carbon steel (450 and 500 MPa accordingly).

All copper alloys are subdivided into two groups: brass and bronze.

Brass

Brasses are alloys of copper and zinc. If a brass does not contain any other alloying element except for zinc, it is a *simple brass*; if there are also other additives in its composition, an alloy is called a *special brass*.

Zinc is dissolved in copper up to 39 % wt., forming an α substitutional solid solution. Addition Zn over 39 % wt. produces β phase CuZn with BCC lattice (the ordered solid solution based on chemical compound). This gives higher strength but accompanied by sharp fall in ductility (Fig. 11.5).

Brasses with zinc content no more than 45 % wt. are applied, as at higher concentration the structure consists of brittle β phase only.

Single-phase, or α *brasses* are ductile metals; the products made of by cold deformation processes. These include any parts feasible by sheet-metal die forging, as well as wire, tapes, radiator tubes, cartridge cases, electro-technical details.

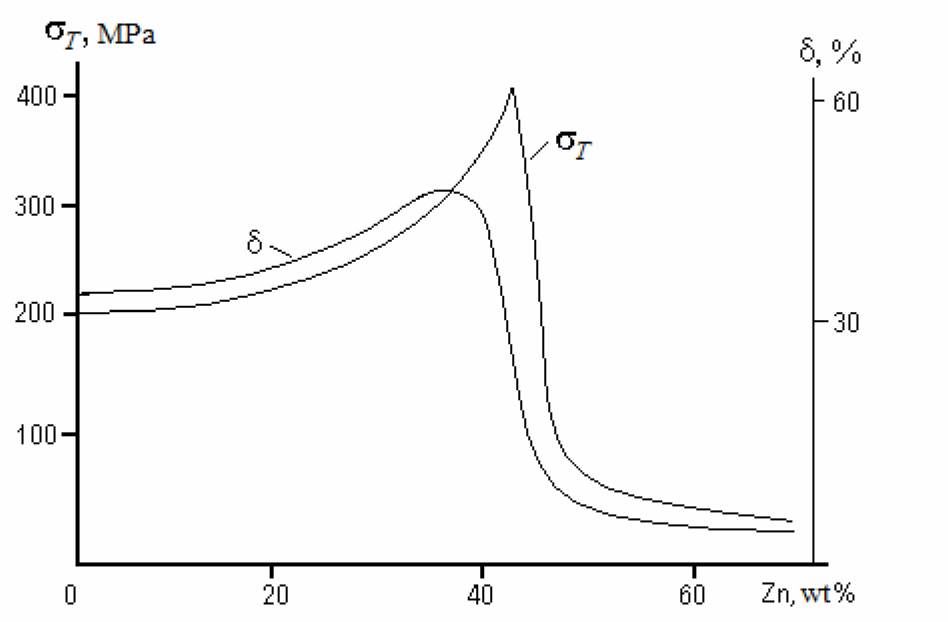


Figure 11.5 Dependence of brass mechanical properties on zinc content

Two-phase, or *(*α + β*) brasses* are stronger and harder, but are less ductile; products are made either by casting or hot plastic deformation. These are various cast and die forged work-pieces which then are processed by cutting (steam and water fitting).

Brass grades denote the copper content, instead of an alloying element (zinc), as opposed by the majority of alloys: Л96 (96 % wt. Cu), Л80 (80 % wt. Cu), ЛАН59-3-2 (59 % wt. Cu, 3 % wt. Al, 2 % wt. Ni, zinc is the balance)[2].

Brass with the zinc content up to 10 % wt. is called *tombac*, or *low brass*, with 10-20 % wt. – *rich low brass*. These ductile alloys of beautiful golden colour are used for works of art and jewelry.

Casting brass with maximum castability and containing 3 % wt. Si is applied for making cast pieces. For parts of sea crafts naval brass with 1 % wt. of tin is used: it is resistant to corrosion in sea water.

Additives of nickel and iron raise strength of brass up to 550 MPa.

The brass keeps plasticity and toughness upon temperatures below 0 °C.

Bronze

Bronzes are alloys of copper with any elements except for zinc. Classic bronze is an alloy of copper and tin below 10 % wt. They are expensive. Bronzes of complex composition are cheaper. For example, antifriction bronze contains 4 % wt. Sn, 4 % wt. Zn, and 2.5 % wt. Pb.

Structure of copper–tin alloys is rather complex and includes solid solutions, intermetallic phases, and products of eutectoid transformation.

By technology of products manufacturing the bronzes are subdivided into *cast bronzes* (for antifriction parts and steam-and-water fitting) and *wrought bronzes* – single-phase alloys (for elastic elements, as membranes and springs).

Aluminum bronze (9-10 % wt. Al) is applied for small vital parts (gear wheels, plugs, flanges, and also medals and coins).

Silicon bronze (3-4 % wt. Si) plays role of a tin bronze substitute, it has high elastic properties and used for making springs.

Lead bronze is an antifriction alloy, it is necessary for making bushings in sliding bearings.

Bronze containing beryllium has very high elasticity and strength: σ_T = 1100-1200 MPa. This alloy is intended for clock and instrument springs, elastic contacts.

Questions and problems

1. Cite classification and characteristic of nonferrous metals.
2. What is aluminum applied for?
3. What groups are aluminum alloys divided into?
4. Describe cast aluminum alloys.

---

[2] Grades designation accepted in Russia

5. Explain the principle of wrought aluminum alloys strengthening.
6. Characterize properties and application of titanium alloys.
7. What are main fields of copper application?
8. What are *brass* and *bronze*? Where are they used?

12. NONMETALLIC STRUCTURAL MATERIALS

12.1. RESTRICTIONS IN METALS PERFORMANCE

Metal structural materials are strong and reliable, technological and in many cases are economically effective. But metals possess, nevertheless, a number of the essential lacks limiting their application.

First, many metals and alloys are subject to corrosion in excited environments. High heat and electric conductivity of metals are not advantages in all cases as heat insulating materials and dielectrics are necessary, too. Metal materials do not always provide necessary hardness and wear resistance under friction conditions. In many cases hot-resistance and fire resistance of metals are insufficient. The strongest metal materials have the high density, i. e. do not allow getting the high unit strength necessary for air craft and the space engineering. At last, the technological route from ore mining to a finished metal product takes very long time, includes huge number of operations and is rather labour-consuming.

Therefore in many cases non-metallic materials are applied. They are usually subdivided into polymers (plastic), ceramics and glass what was told in the chapter 1.

12.2. POLYMERS, OR PLASTICS

Plastic is the artificial solid material made on the basis of organic polymeric binding substances. Have the big molecular weight (above 10,000).

Composition of plastics

1) *Binding material* is an obligatory component. These are synthetic resins or ethers. Simple plastic (organic glass, polyethylene, polypropylene) consist almost of one binding substance.

2) *Filling material*. Content of fillings can reach 70 %. They can be powder (soot, graphite, talc, wood flour), fibrous (cotton, glass, asbestos fibres), sheet (a paper, fabrics, a wood veneer). Fillings raise mechanical strength, reduce cost of plastic and give them the necessary operational properties.

3) *Stabilizers*. They are necessary, that macromolecules of polymers did not change the spatial structure, and properties of plastic did not vary eventually.

4) *Softeners (plastifiers)*. They are added in quantity not more than 20 %. They improve moldability of plastic, reduce brittleness. Usually they are oleinic acid, stearin, dibutylmetaftalat.

5) *Hardeners*. They are added into plastic based of thermosetting resin as catalysts of hardening. These are organic peroxides.

6) *Special additives*. These are dyes, greases, antistatics, additives against burning, against a mildew, etc.

Properties of plastics

Advantages of plastics in comparison with other structural materials are:

- low density;
- high unit strength σ_T/γ;
- chemical firmness;
- electrical insulating properties;
- heat insulating properties;
- less labour input of plastic processing in comparison with processing of metals: a product and a material are created simultaneously;
- less quantity of a waste, than at processing of metals (material utilization rate is not less than 0.9);
- as a rule, finishing operations are not necessary.

Replacement of metal details with plastic ones gives the weight and labour input decrease by 4-5 times, the number of operations is decreased by 5-6 less. The cost price is decreased by 2-3 times.

The main disadvantages of plastics:

- limited thermostability: the maximum temperature of operation for thermoplastics is 250 °C (ftoroplast), and for thermosetting plastics – nearby 400 °C (fiberglass);
- low stiffness and toughness;
- propensity to ageing, i. e. properties change eventually.

Structure of plastics

Structural unit in polymers is the *macromolecule* consisting of huge number of identical groups of atoms – mer units. Each mer unit is the changed molecule of initial low-molecular substance – a *monomer*. In polymer structure molecules of a monomer are united with each other and form long chains in which atoms are connected by covalent bonding.

For example, polymer polyethylene $(–CH_2–CH_2–)_n$ which macromolecules consist of mer units CH_2, is produced by polymerization of n molecules of a monomer, gas ethylen $CH_2=CH_2$. The number *n* makes thousand.

In schemes of macromolecules covalent bonding is shown by a dash: “–“ (see Fig. 12.1).

Properties of polymers are defined not only by a chemical compound, but also by a structure and a relative positioning of molecules.

Linear macromolecules are chains with the relation of length to the cross-section size above 1000 (Fig. 12.2, *a*). They can form zigzags, spirals or to be mixed up. Between macromolecules there is the weak secondary bonding caused by van der Waals forces. Molecules of thermoplastics have such a shape.

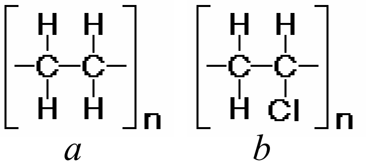


Figure 12.1 Schemes of polyethylene *(a)* and polyvinyl-chloride *(b)* macromolecules

In polymers with the *branched* structure attractive forces between macromolecules are weaker, polymers are less strong (Fig. 12.2, *b*). They are more fusible and friable.

In polymers with a *crosslinked* structure there is covalent bonding between molecules (Fig. 12.2, *c*). They are strong, not fusible, insoluble (can be softened and bulk up only).

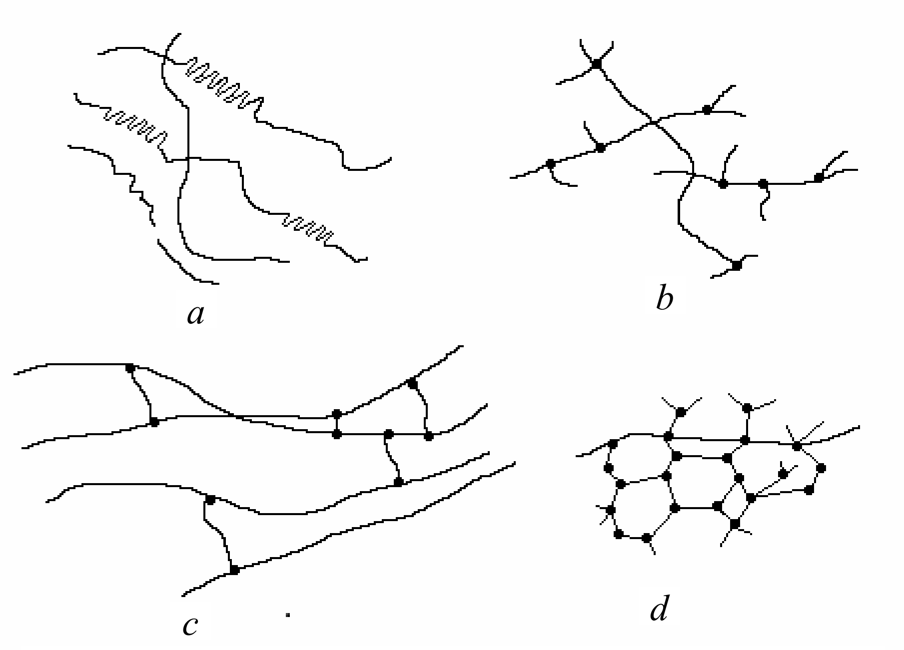


Figure 12.2 Molecular structures of polymers:
a – linear; *b* – branched; *c* – crosslinked; *d* – network

In polymers with a *network* structure all linear sites are connected by cross-section covalent bonding. In this case the product represents a huge spatial molecule (Fig. 12.2, *d*). Such polymers are brittle, thermostable and do not dissolve (not soften and swell). These are thermosetting polymers.

The structure of a linear macromolecule is schematically shown in Figure 12.3.

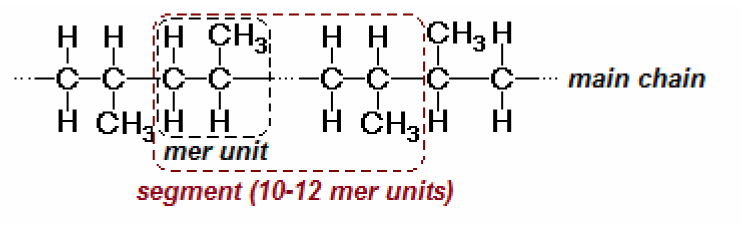


Figure 12.3 Scheme of linear macromolecula

Energy of covalent bonding between atoms in the main chain is great: E_{bond} = 350 kJ/mol. The energy of secondary bonding is approximately 30 times lower. Therefore macromolecules can be shifted with respect to each other rather easily. Besides, a macromolecule is a flexible structural unit since its segments can rotate independently while keeping the valence angle α constant (Fig. 12.4). This is the reason behind the instability of polymers properties: huge flexible macromolecules cannot maintain the set of spatial position for a long time.

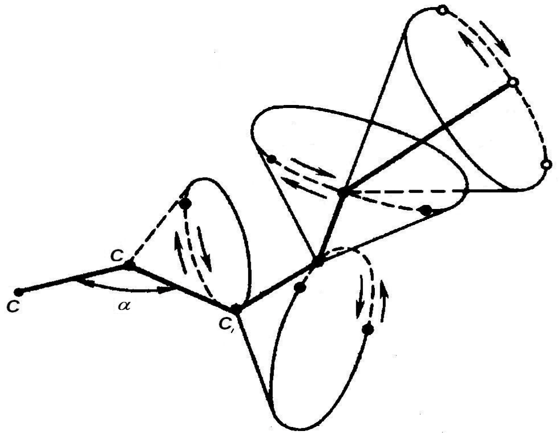


Figure 12.4 Rotation of segments in a macromolecula

Polymers are able to form the ordered arrangement of macromolecules. The ordered structure appears under the influence of attractive forces between molecules and thermal movement of molecules. This phenomenon reduces total internal energy of a system.

One variant of the ordered packing is formation of *chain-packed structures*. *Packs* represent a consecutive arrangement of macromolecules one after another (Fig. 12.5). Packs move as a unit, but become unstable upon heating and stresses applied.

More complex and steady ordered regions are called *crystals*. In the beginning macromolecules fold into tapes at the expense of repeated turns of segments around. Tapes combine into plates which layer and form crystals. In polymer volume there is an alternation of amorphous and crystal regions (Fig. 12.6). Polymer never reaches the absolute crystallization. Crystal polymers are stronger at loading and heating.

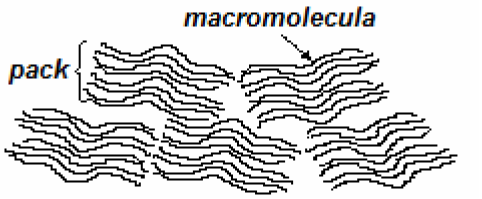


Figure 12.5 Chain-packed structure

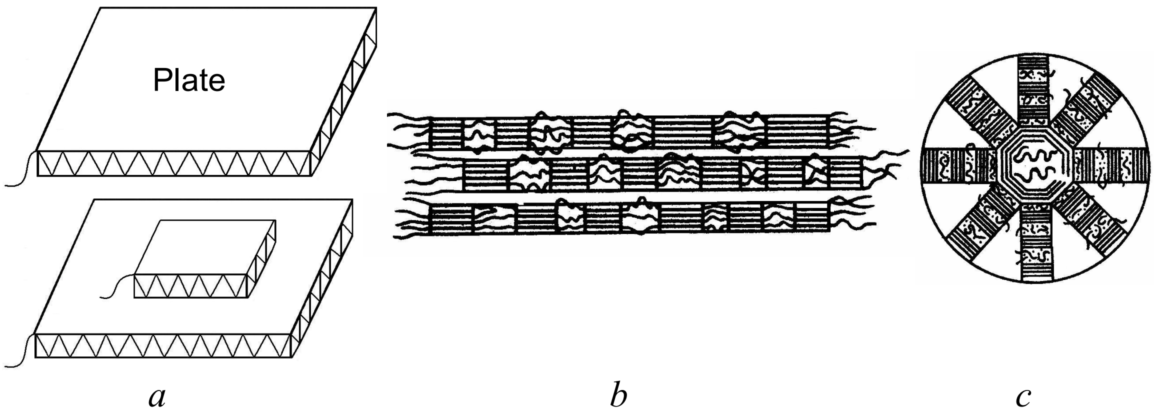


Figure 12.6 Various crystal shapes:
a – crystal formation from plates; *б* – fibrillas; *в* – spherolith

Polymers behavior upon heating

Thermomechanical curves (at constant stress and speed of heating) show deformation value ε versus temperature.

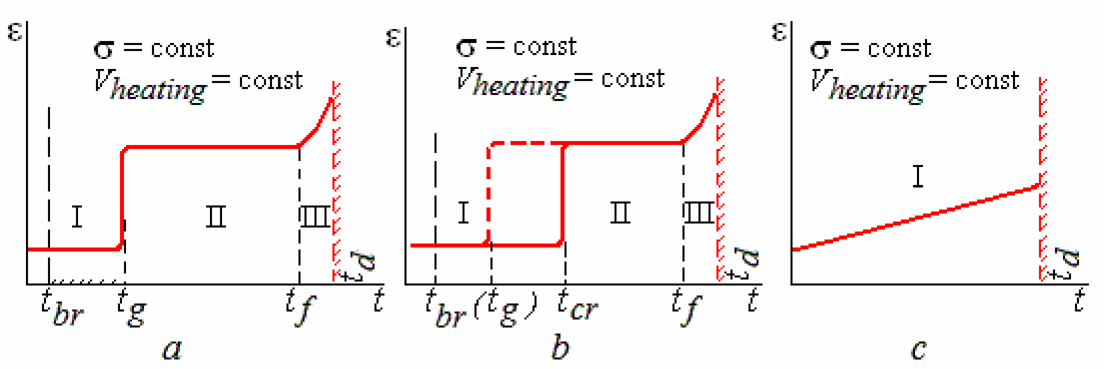


Figure 12.7 Thermomechanical curves:
a – amorphous thermoplast; *b* – crystalline thermoplast;
c – thermosetting polymer

In Figure 12.7, *a* the behaviour of amorphous thermoplastic polymer upon heating is shown. At low temperatures polymer is in *glassy state* (field I) and behaves as an elastic solid body. Then heating translates it into a *viscoelastic* state (field II). Here the polymer strain degree can reach hundreds percent (800 % for rubbers), but it is reversible. Upon the further heating polymer behaves as a *viscous liquid* (field III). Deformation is irreversible. It is an area of plastics processing. Above temperature of thermal decomposition of polymer t_d covalent bonding in macromolecules are broken off, low-molecular compounds deposit, and polymer decomposes. However upon cooling thermoplasts have a polymerization, structure and properties of polymer are restored.

Figure 12.7, *b* shows behaviour of the thermoplastic polymer capable of crystallisation. Below the crystallisation temperature t_{cr} polymer has the ordered structure, above this temperature it transforms to amorphous state. As it is necessary to spend energy for destruction of crystal structure, crystal polymer becomes viscoelastic absorbing more heat as compared to amorphous one.

In Figure 12.7, *c* the behaviour of thermosetting polymer when heated is shown. It is capable of deforming slightly only in elastic area, and then, upon heating above t_d, it decomposes irreversibly. When cooled, polymerization does not occur, properties are not restored.

Area of working temperatures for polymer lies below the *glass transition temperature* t_g though it can work for a short time above this temperature. But it is necessary to consider that below the *brittleness temperature* t_{br} polymer fractures in a brittle manner (a stress value necessary for starting deformation exceeds tensile strength). Thus, polymer works reliably under loading in the range of temperatures from t_{br} to t_g. The wider this interval the better it is for plastics.

It is necessary to understand that temperatures of polymer transitions from one state to another are not constants (for example, t_g and t_f – *fluidity temperature*). They depend on conditions of loading. The higher is the strain rate, the higher are these temperatures. It is the feature that differs plastics from alloys.

Polymers behavior under loading (stress-strain diagrams)

Amorphous linear polymer in a glassy state is capable for big enough elastic strain degree – up to 20 % (field I in Fig. 12.8, *a*). Polymers have their modulus of elasticity *E* (tg α) much lower as compared to metals. Viscoelastic strain may achieve hundreds percent (Fig. 12.8, *a*, field II). It occurs on the account of unbending the folded macromolecules. Further more intensive loading leads to the displacement of macromolecules with respect each other. It is viscous liquid state (Fig. 12.8, *a*, field III).

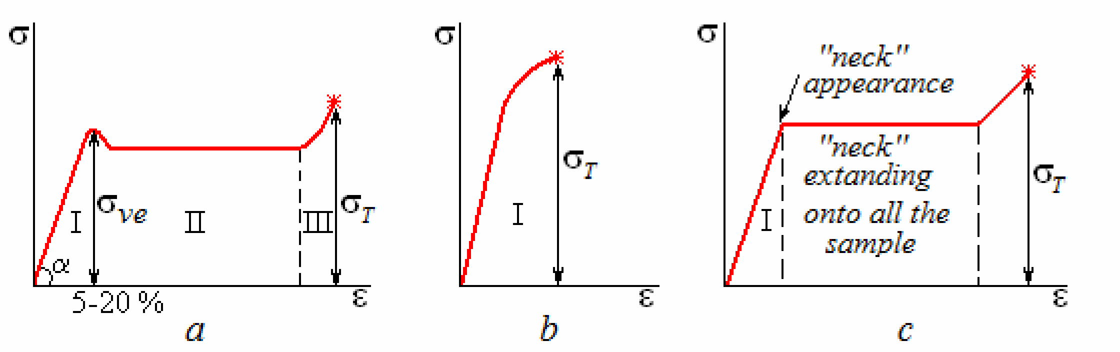


Figure 12.8 Stress-strain diagrams for polymer materials:
a – amorphous thermoplast; *b* – thermosetting polymer; *c* – crystalline thermoplast

Under mechanical loading and before destruction, polymer passes through the same stages as those existing during heating. However, the energy needed for transition to a new state is acquired from the deformation work instead of the heat source.

Thermosetting polymer with network structure is capable of experiencing only elastic deformation until the moment of destruction (Fig. 12.8, *b*). Such polymers have the higher stiffness E and strength σ_T than thermoplasts.

Crystalline polymer at temperature below t_{cr} after uniform elastic deformation (Fig. 12.8, *c*, field I) forms local narrowing called “neck” which gradually extends onto the whole sample. Thus there is a change of crystal structure fixing the residual strain. Stiffness and strength of crystalline polymer is higher that of the same polymer in amorphous state.

12.3. CERAMICS

Ceramics is the inorganic solid materials produced by high-temperature burning from formed mineral mixtures. It is possible to say that the ceramics is all the materials which are not polymers and metals. In ceramic materials there is either covalent or ionic bonding between the atoms.

For ceramics production there is a large quantity of natural compounds; they make up to 85 % of earth crust. The content of silicon only is about 40 %. In the Tomsk region there are own resources for ceramics manufacture such as alumina in Achinsk, the Tugansky deposit of zirconium sand.

The modern engineering uses more than 7000 various products made of ceramics starting from ferrite of size about a pin head and thin films for touch devices to huge insulators for electric power lines.

Ceramics structure

Basis of *building*, *household* and *art ceramics* is natural clay. The *technical ceramics* has more homogeneous structure; it is made from oxides or oxygen-free compounds.

While burning (1200-2500 °C) structure and properties of ceramic materials are formed simultaneously. Ceramics always is

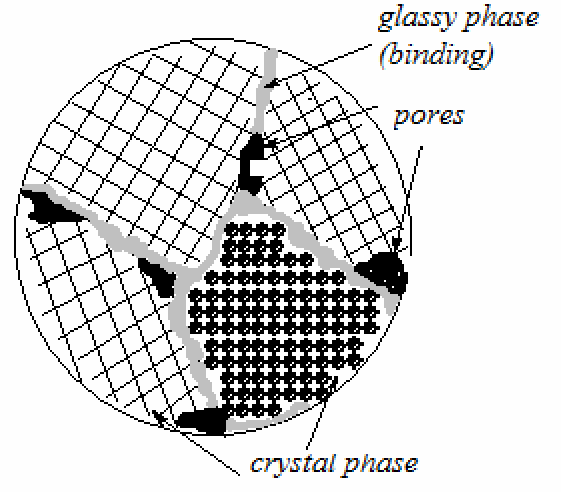


Figure 12.9 Ceramic structure

multiphase substance: it contains crystal, glassy and gas phases in various proportions (see Fig. 12.9).

Crystal phase represents chemical compounds or solid solutions. It is the basic part of structure and defines strength, hot-resistance and other major properties of ceramics.

Glassy or amorphous phase is a binder; its quantity can vary largely: from 1 to 40 %. It reduces strength and hot-resistance, but facilitates the technology of production.

The gas phase is in ceramics pores. By the volume content of pores the ceramics is subdivided into *porous* and *dense*. For engineering purposes the dense ceramics is more often used. But also it contains a certain share of pores.

Properties of ceramics

Advantages of ceramics are:

- high hardness and wear resistance;
- high working temperatures (to 3500 °C);
- high corrosion resistance in various environments;
- low heat and electric conductivity: ceramic materials are dielectrics and heat insulators;
- low density; ceramics are rather light materials.

The basic lack of ceramics:

- high brittleness. Impact strength of ceramics is approximately 40 times less, than metals have. Brittleness limits its application in the technique. The ceramic goods have low strength under stretching and bending. Ceramics does not plastically deform.

High strength and melting temperature of ceramic materials are caused by high energy of interatomic bonds. These are either covalent or ionic compounds. Strong interatomic bond defines high resistance to deformation, therefore special strengthening processing is not required for ceramics.

To increase the impact strength of ceramics, there are various approaches. First of all, the amount of pores in a ceramic material should be as low as possible because they are sources of cracks. For today, the following basic methods of improving the fracture toughness of ceramics are developed:

- alloying or modifying,
- strengthening by disperse particles,
- strengthening by whiskers of stronger ceramics,
- “blunting” of cracks at the expense of set of microcracks creation: in this case the main crack does not develop.

To find a solution to this actual problem of improving the resistance to fracturing (toughness) of ceramics, materials scientists are working all over the world including Tomsk scientists at the Institute of Strength Physics and Materials Science SB RAS.

Ceramics classification and application

The technical ceramics can be subdivided into 3 groups: oxide ceramics, oxygen-free ceramics and metal ceramics (cermets).

1) *Oxide ceramics* is made from oxides of various elements: Al, Mg, Zr, Si, Be, U. It consists basically of a crystal phase and pores. The glassy phase appears only at the expense of impurity.

Oxide ceramics is hard, fire-resistant, and chemically resistant in acids, alkalis, on air. Working temperatures make 0.8-0.9 of the fusion temperatures 2000 to 3300 °C. But it does not withstand the sharp changes of temperature.

The porous ceramics of this group is applied as heat insulator material and fire-resistant lining for chambers of combustion, metallurgical furnaces and ladles (silica, magnesite, fireclay bricks). The foam ceramic thermal protection of space shuttle “Buran” had only 5 % of a material and 95 % of pores filled with inert gas. Porous ceramics is applied also for making filters for various liquids (water, wine, oil).

Ceramics based on aluminum oxide Al_2O_3 is called *emery*. It is applied in the most different areas of engineering:

- radomes of radar scanners,
- bearings for furnace rollers,
- inputs and supporting devices for heaters in thermal furnaces,
- electroinsulators,
- nozzles of argon-arc torches, spray jets for water injection into a well (pressure 15 MPa), sandblasting and shot-blast units,
- dies for wire drawing,
- thread carriers in the textile industry,
- cutting tools,
- distributors and washers in the household sanitary technician,
- face seal rings for pumps.

The ceramics based on zirconium oxide ZrO_2 has very important feature. ZrO_2 experiences 3 polymorphic transformations when heated: the monoclinic lattice turns into tetragonal, and then to the cubic. The tetragonal lattice can be stabilized at low temperatures by means of modifying. In this case, the phase transformation begins at the expense of the applied stress. Such modified ceramics has a tensile strength 3000 MPa together with criterion of crack resistance K_{1C} = 20-25 (for ordinary ceramics it is not higher 4). ZrO_2 is used for solid-oxide fuel cells (for electric power generation), gauges of the oxygen content in molten steel.

In instrument making, the electrical engineering and electronics the so-called *fine ceramics* is applied. It is dense and fine-grained (the size of grains 1-5 μm). These are, for example, ferrites – high-frequency magnetically soft materials from iron oxides $FeO{\cdot}Fe_2O_3$, sintered or melted into a single crystal without pores. Magnetically hard ferrites also exist. Electrical porcelain ceramics is applied for insulators. There is a special condenser ceramics (ultra porcelain, steatite TiO_2) with high value of dielectric permeability ε.

2) *Oxygen-free ceramics* are carbides Me_xC_y, nitrides Me_xN_y, borides Me_xB_y, etc. These are refractory compounds, their fire resistance reaches 3500 °C. Hardness comes nearer to hardness of diamond. They possess high wear resistance and heat resistance.

Silicon carbide SiC is a hard, chemically resistant, light, heat resisting material. It is used for heaters of furnaces, thermowells, blades of gas turbines, parts of internal combustion engine, grinding circles, coatings on graphite.

Silicon nitride Si_3N_4 is resistant in the fused metals and slags. It is applied for parts of gas turbines, heat resisting tools, crucibles, crystallizers, parts of pumps for pumping of the fused metals.

3) *Metal ceramics,* or *cermets,* are manufactured by mixing of powders of refractory ceramic compound and metal. Then the mixture of powders is pressed and sintered. Metal plays a binding role; it improves both plasticity and toughness. Thus the flexure toughness σ_T increases, too. The binders are made of cobalt, nickel, iron, molybdenum. The ceramic component can be both oxide and oxygen-free types.

Metal ceramics are widely applied for cutting hard alloys. Also they are used for manufacturing cutting plates for mills, drills and cutters; and also stamps, dies, the boring tools. They consist of carbides WC, TiC, TaC and cobalt for binder. Cermets Cr_7C_3 – Ni, Al_2O_3 – Cr, BeO – W are applied as heat resistant materials.

12.4. COMPOSITE MATERIALS

Composite materials (composites) relate to a new class of light and high-strength materials with the high resistance to crack propagation.

Composites surpass all traditional constructional materials in specific strength and specific stiffness. Besides, they retain high strength at elevated temperatures and resist to failure by fatigue.

Composites are complex materials made of components whose structure and properties are strongly different. They are not soluble in each other and separated by clearly marked boundary.

The principle of composite structure is borrowed from nature: trunks of trees consist of rigid cellulose fibres and soft lignin, bones of the humans and animals are constructed from rigid threads of phosphate salts and soft, viscous protein collagen.

Properties of composite materials depend on properties of components and bond strength between them. Characteristic feature: composites show advantages of components, instead of their lacks. In addition, composites have properties not revealed by any of their component. Therefore composites' components with properties supplementing each other are chosen.

Structure of composites

The composite material consists of a basis, or a *matrix* (metal or polymeric) and a *filler*, or a reinforcing component.

The matrix binds a material in a single whole, forms it. The technology of material manufacture involving working temperature, specific strength σ_T/γ, and fatigue strength σ_{-1} depend on the properties of the matrix.

The filler is distributed in a matrix uniformly in a certain order. The filler takes up a load; therefore it should have high strength, hardness and elastic modulus.

The matrix distributes loading between particles of the filler, protects their surface and raises the energy of crack propagation to prevent brittle failure. The matrix is not strengthened; it is the difference of composites from metal alloys.

By their shape, the fillers can be zero-dimensional, one-dimensional and two-dimensional (Fig. 12.10).

The composite materials strengthened by small particles of filler, are called *dispersion-hardened* materials. The composites containing fibres are named *fibrous* composites. Two-dimensional fillers are applied, basically, in polymeric composites.

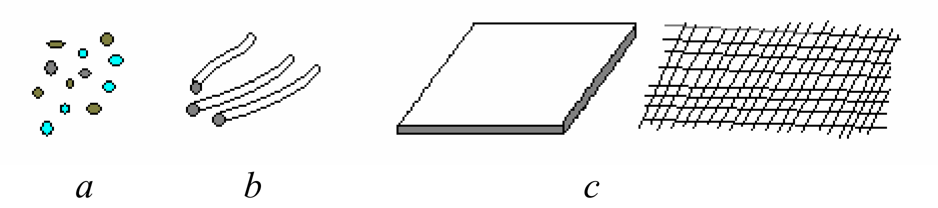


Figure 12.10 Shape of fillers in composites:
a – particles; *b* – fibres; *c* – plates, sheets, fabric

Dispersion-hardened composite materials

The fillers are particles of refractory substances: oxides, carbides, nitrides. Usually they are Al_2O_3, SiO_2, BN, SiC.

Materials with low density (aluminum, magnesium, titanium and their alloys), or heat resisting materials (nickel) are applied for matrixes.

Dispersion-hardened composites are obtained by pressing and sintering or by introduction of filler into a liquid matrix before casting.

In this kind of composites the matrix carries the basic loading, and particles of filler disturb to movement of dislocations. For them the following relation is valid: $\Delta\sigma_Y \sim \frac{1}{R}$, where R is a distance between particles of filler. The best combination of mechanical properties is reached if the size of particles is 0.01-0.1 µm and distance between them is equal to 0.05-0.5 µm.

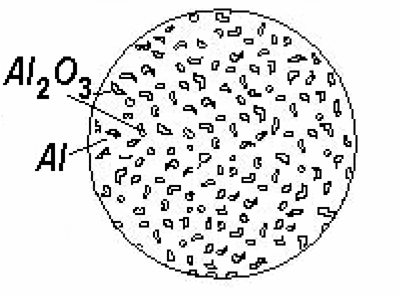


Figure 12.11 Structure of sintered aluminum powder

Example of dispersion-hardened composites is sintered aluminum powder (SAP). It has high heat resistance and corrosion resistance. It consists of aluminum metal matrix and very thin alumina flakes (0.1-0.2 µm thick), as shown in Figure 12.11. The more the share of alumina Al_2O_3, the higher strength, hardness and heat resistance, but lower plasticity (Fig. 12.12).

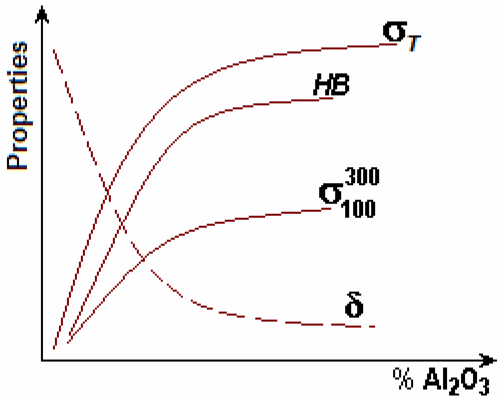


Figure 12.12 Dependence of SAP mechanical properties on oxide share

Advantages of such material in comparison with ordinary aluminum alloys are very fine grains, uniform distribution of strengthening particles, absence of linear defects.

Products made of SAP are: sheets, foils, rolled shapes, pipes. Parts made of SAP are intended to work at 300-500 °C: blades of compressors, turbines and fans.

Fibrous composite materials

The fillers for this group of composites are fibres or threadlike crystals. Filler materials are carbon, boron, SiC, Al_2O_3, glass, and also wires made of stainless steel, molybdenum, tungsten, and beryllium. Fibres are the elements taking up loading. For matrixes the same metals, as for the previous group are used.

To achieve the maximum strength of composite material, the fibres should be aligned in the direction parallel to the stress action. Therefore the arrangement of fibres can be single-axis, biaxial or three-axial (see Fig. 12.13).

For single-axis reinforcing, the anisotropy appears so that in the direction of fibres strength is higher than in transversal direction (because the load is carried by a fibre, and a matrix is the transmitting medium). For biaxial reinforcing the anisotropy is not present, but strength along an axis of fibres reduces by a factor of 3 approximately (Fig. 12.14).

The thinner and longer is a fibre, the higher is the strengthening degree (see fig. 12.15).

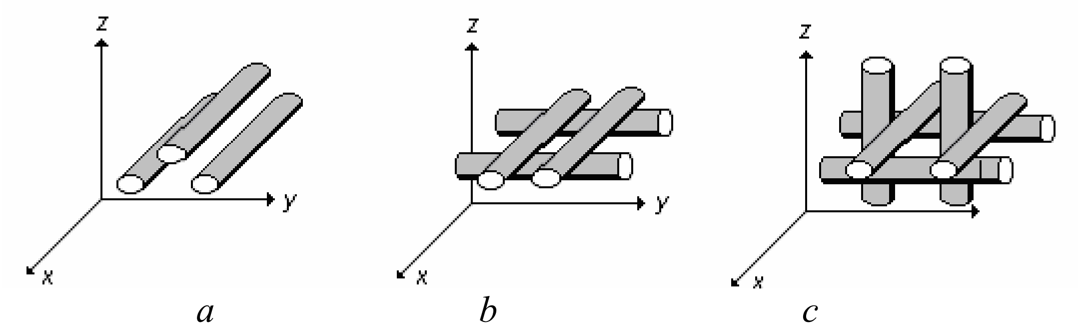


Figure 12.13 Arrangement of reinforcement fibres in composites:
a – single-axis; *b* – biaxial; *c* – three-axial

The volume fraction of fibres makes from several percent to 80-90 %. The increase in filler content serves to enhance the strength and other characteristics.

For example, composite consisting of aluminum and boron fibres has tensile strength at a level of 1200 MPa (as carbon steels have), and specific strength much more exceeding that of steels.

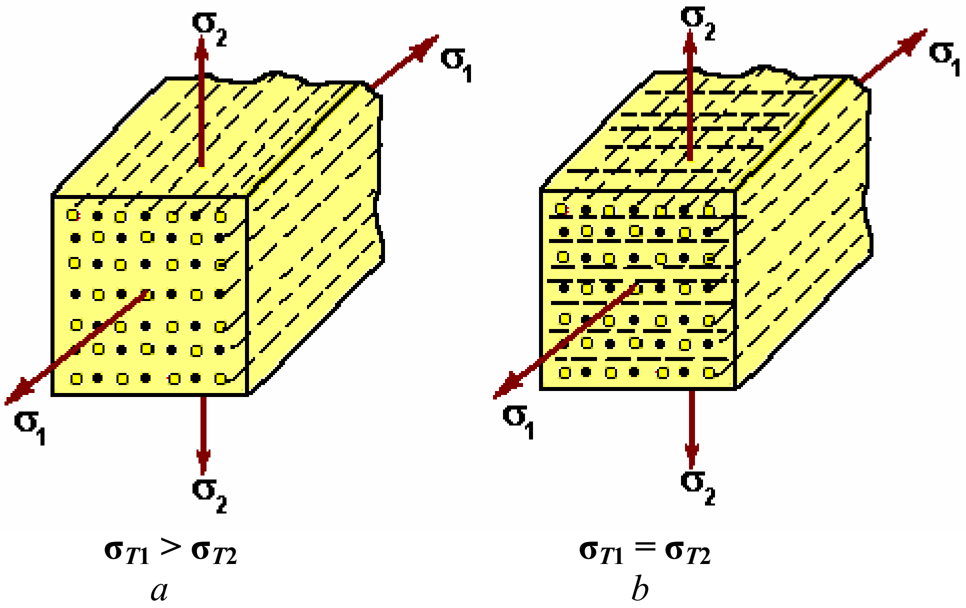


Figure 12.14 Strength at single-axis *(a)* and biaxial *(b)* reinforcement

Fibrous composites are manufactured by forming the fibres in a matrix powder, fibre impregnation by liquid metal of a matrix, matrix deposition onto fibres with the subsequent formation and sintering and by other ways. The method of directed crystallisation of eutectics is more and more applied too.

Problems of composites technology is that fibres of boron, carbon, silicon carbide and others badly stick to the matrix and are not wetted by liquid matrix metal. Good adhesion is provided by diffusion processes and chemical reactions (usually intermetallic phases form on a boundary matrix-fibre). It is necessary to apply various methods, for example, to put preliminary metal coverings on fibres which improve adhesion, but doing so will increase the costs of material. Sometimes etching the fibre surface helps. It improves bonding with matrix metal. On the surface of boron or carbon fibres single crystals of silicon carbide SiC are grown up, and fibres become fleecy. It is possible to grow boron crystals on the surface of thin 12 μm diameter tungsten wire. All fibres will have diameter 70-200 μm. Such fibres are more strongly bonded to a matrix.

The basic disadvantage with the fibrous composites is their high cost and complicated production.

Carbon fibres are slightly cheaper. They are produced from synthetic organic fibres by high-temperature processing. They can be made in the form of yarns, threads, a fabric, tapes. Each fibre consists of the smallest ribbons – fibrillas.

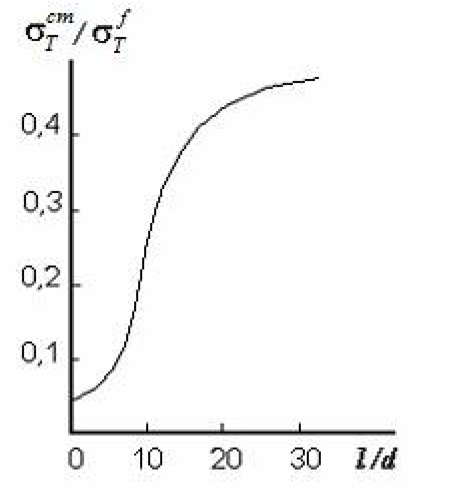


Figure 12.15 Dependence of composite strengthening degree on ratio *l*/*d* of filler: *l* – fibre length; *d* – fibre diameter

Glass fibres can have square, rectangular, hexagon shape for the best packing in a matrix.

Composites application increases every year. The main consumers are aircraft, rocket and space techniques. Light and strong casings, combustion chambers of rocket engines, blades of turbines and screws, body parts of cars are made of them.

The major part of a turbine is a blade made of a nickel alloy and strengthened by threads of sapphire Al_2O_3, such a component serves to maintain the temperature of input gases as high as 1650 °C! The tensile strength of threads is higher than 700 MPa.

Nozzles of rockets are made of tungsten or molybdenum powders with ceramic threads Al_2O_3 in the shape of fibres or felt to increase their strength by a factor of 2.

Composite materials with polymeric matrix

In composites based on polymers, the load is transferred from a matrix to the reinforcing fibre at the expense of adhesive intermolecular interaction forces. Full wetting of fibres' surfaces by liquid binding is necessary.

Boron and carbon fibres are better wetted with epoxy resin. *Boron* and *carbon plastics* are produced with this matrix.

Glass-fiber plastics have the maximum strength and specific strength as follows: σ_T is equal to 700 MPa and even 2400 MPa (if reduce fibres diameter and add single crystals of Al_2O_3 to a matrix).

Composites are joined by spot welding, gluing, using combination of gluing and bolting or riveting.

Questions and problems

1. What groups of non-metallic structural materials are used in machine building?
2. Cite the restrictions in metals and alloys application.
3. Analyze advantages and disadvantages of plastics as a structural material (compare with metallic materials).
4. Compare the structure and properties of *thermoplastic* and *thermosetting polymers*.
5. How the crystal structure in polymers is arranged?
6. Describe behaviour of polymers upon loading and heating.
7. Structure, properties and application of *ceramics*.
8. What is inorganic glass? How to manufacture it? Where is it used?
9. What are crystalline glasses? How to obtain them? Where are they used?
10. Give the definition to *composite materials*. Describe the characteristic features of composites.
11. What are *matrix* and *reinforcement*? What materials are used in the capacity of matrix and reinforcement?

REFERENCES

1. Callister, William D. Materials Science and Engineering. – 2000, John Wiley & Sons, New York, USA.
2. Ashby, Michael F. and Jones, David R.H. Engineering Materials 1: An Introduction to Properties, Application and Design. – 2005, Elsevier Butterworth-Heinemann, Oxford, United Kingdom.
3. Ashby, Michael F. and Jones, David R.H. Engineering Materials 2: An Introduction to Microstructures, Processing and Design. – 2006, Elsevier Butterworth-Heinemann, Oxford, United Kingdom.
4. Gregory S. Rohrer. Structure and Bonding in Crystalline Materials. – 2004, Cambridge University Press, United Kingdom.
5. Timings, R.L. General Engineering. – 1995, Longman, Grate Britain.
6. Shigley, J.E., Mischke C.R. Mechanical Engineering Design. – 2001, McGraw-Hill, New York, USA.
7. Егоров Ю.П., Лозинский Ю.М., Роот Р.В., Хворова И.А. Материаловедение: учебное пособие. – Томск: Изд-во ТПУ, 2010.
8. И.А. Хворова. Материаловедение. Технология конструкционных материалов: учебное пособие. − Томск: Изд-во ТПУ, 2011.
9. Лахтин Ю.М., Леонтьева В.П. Материаловедение: учебник для студентов машиностроительных специальностей ВУЗов. – М.: Машиностроение, 2008.
10. Арзамасов Б.И., Сидорин И.И. и др. Материаловедение: учебник для высших технических учебных заведений. – М.: Машиностроение, 2005.
11. http://techlibrary.ru/
12. http://www.materialscience.ru/subjects/materialovedenie/knigi/
13. http://www.docload.ru/
14. http://nayilz.narod.ru/PorMet/
15. http://www.naukaspb.ru/spravochniki/Demo%20Metall/predisl.htm

Educational Edition

Национальный исследовательский
Томский политехнический университет

ХВОРОВА Ирина Александровна

МАТЕРИАЛОВЕДЕНИЕ

Учебное пособие

Издательство Томского политехнического университета, 2012
На английском языке

Published in author’s version

Science Editor Doctor of …,
Professor *Name*
Typesetting *Name*
Cover design *Name*

**Printed in the TPU Publishing House in full accordance
with the quality of the given make up page**

Signed for the press 00.00.2012. Format 60x84/16. Paper “Snegurochka”.
Print XEROX. Arbitrary printer’s sheet 12.32. Publisher's signature 11.16.
Order XXX. Size of print run XXX.

nqa.
ISO 9001
Registered

Tomsk Polytechnic University
Quality management system
of Tomsk Polytechnic University was certified by
NATIONAL QUALITY ASSURANCE on BS EN ISO 9001:2008

UKAS
QUALITY
MANAGEMENT
015

TPU PUBLISHING HOUSE. 30, Lenina Ave, Tomsk, 634050, Russia
Tel/fax: +7 (3822) 56-35-35, www.tpu.ru