5
Tribological Materials

Today, a choice of some 40 000–80 000 materials is available to the design engineer. Over the historical development of materials engineering, a shift in the preferably used materials can be observed, which is taking place at an increasing rate (Figure 5.1). This chapter provides only a very brief overview, in the form of material groups that have gained importance in tribological systems, the aim being to explain the most important terms and definitions from the point of view of tribology.

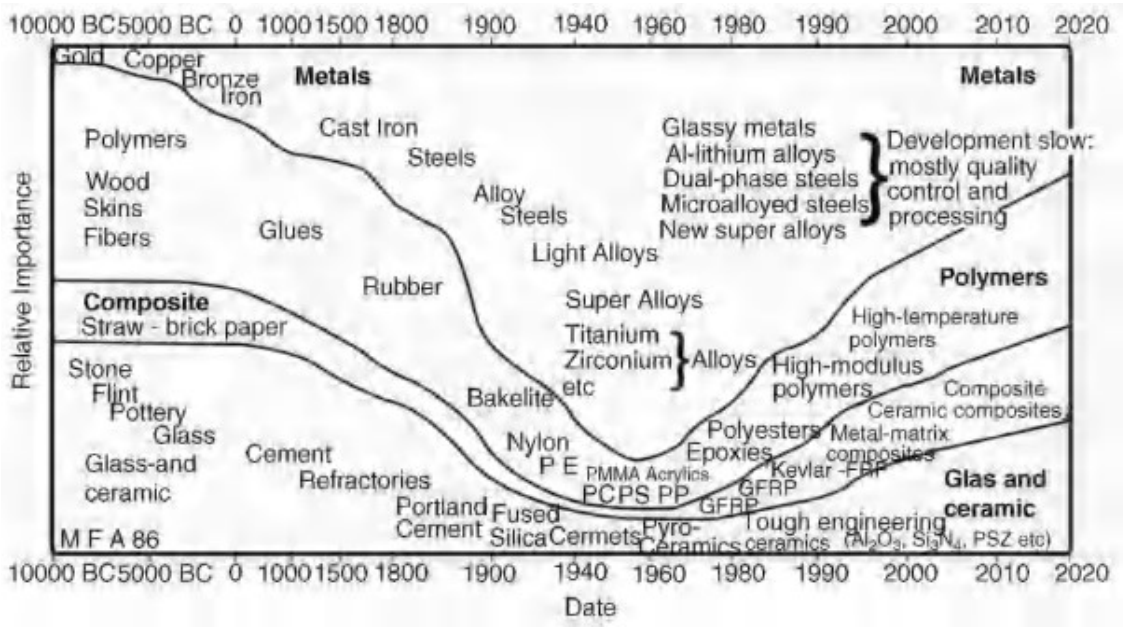


Figure 5.1 The evolution of engineering materials with time. "Relative Importance" in the stone and bronze ages is based on assessments of archaeologists; that in 1960 is based on allocated teaching hours in UK and US universities; and that in 2020 on predictions of material usage in automobiles by manufacturers. The time scale is nonlinear. The rate of change is far faster today than at any previous time in history [1].

Industrial Tribology: Tribosystems, Friction, Wear and Surface Engineering, Lubrication
Theo Mang, Kirsten Bobzin, and Thorsten Bartels
Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
ISBN: 978-3-527-32057-8

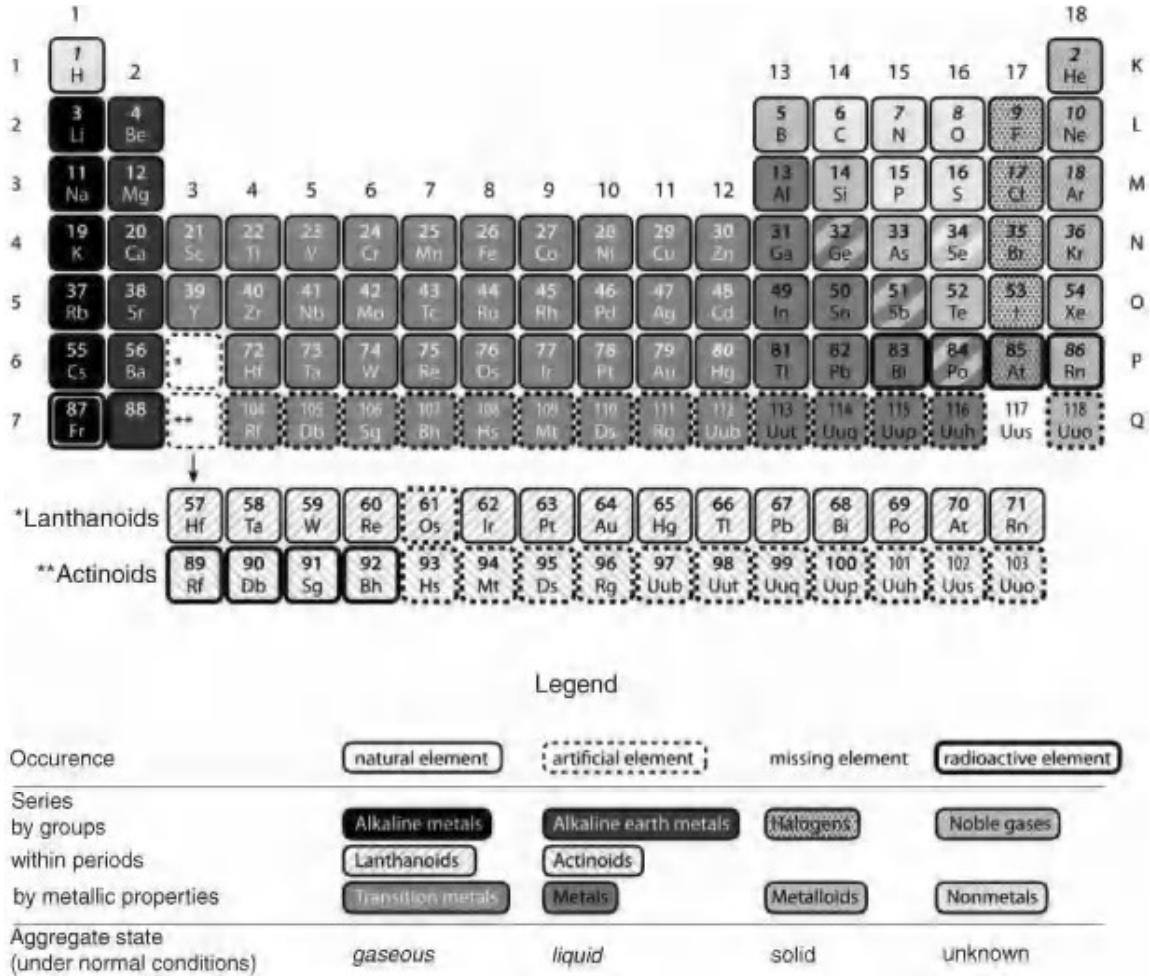


Figure 5.2 The Periodic System of the elements.

Beginning with the basic chemical element (Figure 5.2), the chapter deals with important material properties, such as the lattice structure, the melting point, and the modulus of elasticity, as these parameters decisively influence the tribological properties such as strength, hardness, and material behavior at high temperatures. In consideration of environmental and resource protection, the use of lightweight materials is becoming increasingly important for the design of moving parts; thus, the materials' densities are also of interest. The most important alloy concepts will also be discussed.

Comprehensive data collections for the selection of materials have been compiled above all by Michael F. Ashby (e.g., "Materials Selection in Mechanical Design" [1, 2]), on the basis of which he has developed material identification cards, for example, for the ratio of the modulus of elasticity to the density (Figure 5.3) or of the fracture toughness to the strength (Figure 5.4).

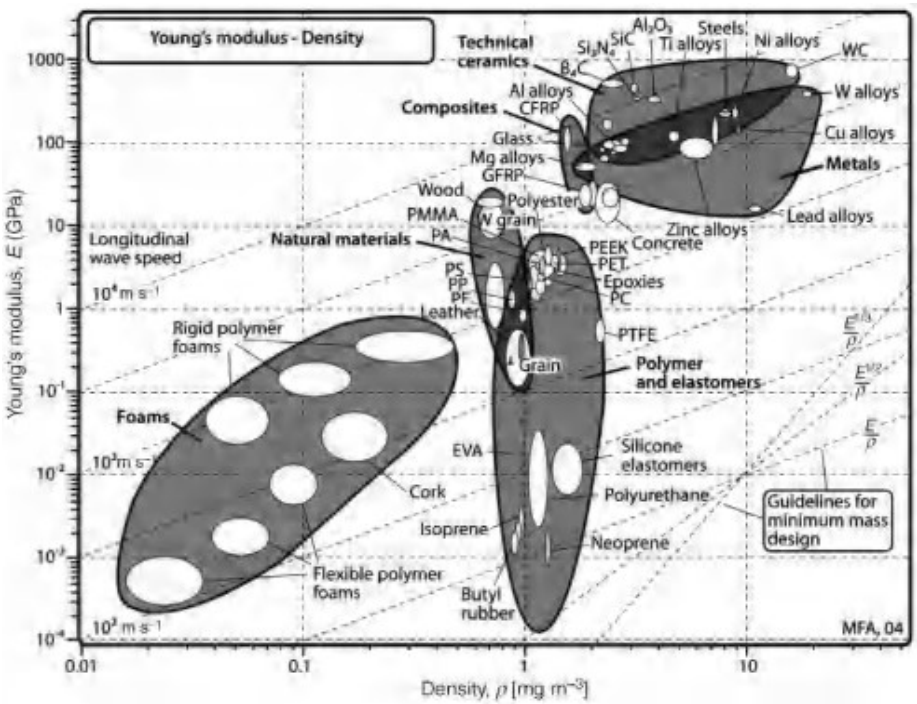


Figure 5.3 Young's modulus E, plotted against the density ϱ. The lines of constant E/ϱ, $E^{1/2}/\varrho$ and $E^{1/3}/\varrho$ allow selection of materials for minimum weight, deflection-limited, design [2].

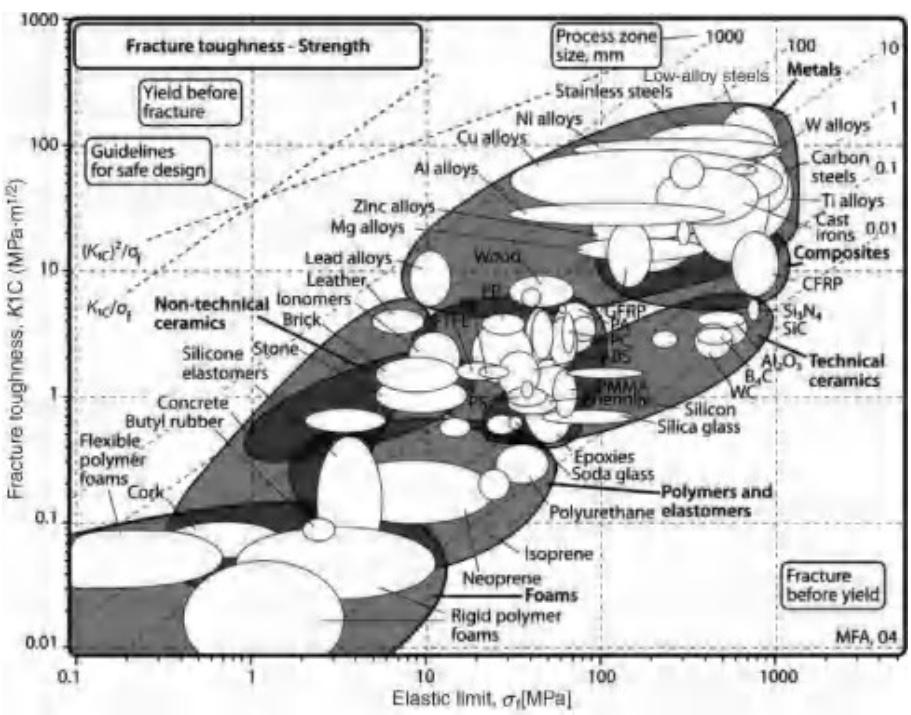


Figure 5.4 Fracture toughness K_{IC} plotted against the failure strength σ_f. The contours show the value of $K_{IC}^2/\pi\,\sigma_f$ – roughly, the diameter of the process zones at a crack tip. The design guidelines are used in selecting materials for damage-tolerant design [2].

5.1
Basic Principles of Materials Science

Compared with metallurgy, the materials science treatment of ceramics and polymers is relatively new. In their basic relationships, however, metals, ceramics and polymers can be largely described within a single framework, which can essentially be derived from the basic principles of metallurgy [3]. For the design of tribological components, above all, the strength properties and the behavior of the material at higher temperatures are of importance, and these will be discussed here in general terms.

5.1.1
Influencing the Strength Properties

The term "strength" refers to the resistance of a material to a change in shape, arising from its atomic structure and micro-structure. The mechanical loading which can cause a change in shape may be in the form of radial and axial stresses, shear stresses and tangential stresses, as well as torques and bending moments. Pressure applied to all sides can also cause deformation. A distinction can be made between elastic deformation (which is completely reversible when the loading is removed, allows only very limited deformation, and follows Hooke's law), and plastic deformation, which is irreversible. There is no linear relationship between the change in shape and deformation. The mechanical properties of materials are influenced not only by their composition, but also to a large extent by the state of their microstructure – that is, the crystal structure, grain size, grain form, and type and density of lattice defects (Table 5.1).

According to loading requirements, strength properties are demanded of technical materials which concern both the entire cross-section of the component and only certain zones, for example, the surface. According to the composition of the material, in addition to its state, temperature, form of loading and loading velocity, several different strengths can be achieved. The technically relevant static strength parameters are determined from the stress–strain diagram (Figure 5.5), which is compiled from tensile tests with standard samples (DIN 50 125). The tensile test

Table 5.1 Lattice defects according to their spatial extent.

Point defects (0-D)	Line defects (1-D)	Planar defects (2-D)	Bulk defects (3-D)
• Vacancies • Interstitial atoms • Interstitial impurity atoms • Substitutional impurity atoms	• Screw dislocations • Edge dislocations	• High-angle boundaries • Low-angle boundaries • Twin boundaries • Phase boundaries	• Voids • Clusters

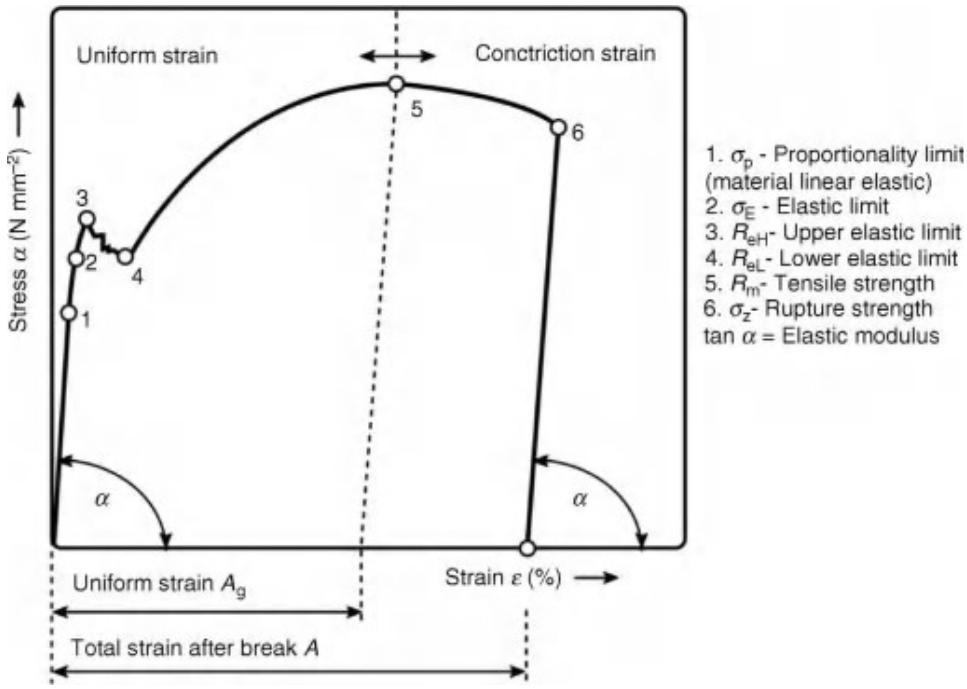


Figure 5.5 Schematic representation of a stress–strain diagram (e.g., for soft steel).

itself is used predominantly for metallic materials and polymers, and is standardized in DIN EN 10 002. For brittle materials, such as glass and ceramics, as well as cast iron, the bending test or compression test is preferentially employed. Important terms are:

Elasticity:	Linear relationship between stress and strain, reversible
Modulus of elasticity E:	Constant of proportionality between normal stress σ and strain ε
Shear modulus G:	Constant of proportionality between shear stress τ and shear strain γ
Hooke's law:	$\sigma = E\,\varepsilon$ or $\tau = G\,\gamma$
Poisson number ν:	(also Poisson's ratio) – Ratio of cross-section diminution to elongation under tensile stress. Here: $E = 2 \cdot (1 + \nu)\,G$ (approximate values: metals $\nu \approx 0.3$; ceramics $\nu \approx 0.25$; thermoplastics $\nu \approx 0.35$)
Yield point:	Stress above which plastic deformation occurs, that is: yield strength for tensile loading compressive yield point for compressive loading torsion limit for torsional loading
Strength:	Resistance to plastic deformation
Ductility:	Capability for undergoing plastic deformation
Toughness:	Resistance to the propagation of cracks or fracture

In contrast to an ideal crystal, for a real crystal the critical shear stresses are two orders of magnitude lower. Whereas, an ideal iron crystal has a strength of 28 000 MPa, real technical pure iron has a strength of only 240 MPa. The reason for this is to be found in the lattice defects of a real crystal, above all screw dislocations and edge dislocations. Notably, real crystals grow with dislocations, which further propagate during plastic deformation (Frank–Read sources); assuming that the plastic deformation takes place primarily due to the migration of dislocations along the slip planes of a crystal lattice, then in principle two methods are available for improving the strength in a real component:

1) Reducing the dislocation density, and thus approximating the ideal crystal. Technically, this is realized with fibers and whiskers, which must have a diameter of $D \leq 1$ μm, because dislocation-free zones occur for this order of magnitude. Normally, per μm^2 there exists one penetration point of a dislocation line. Fibers and whiskers are used in composite materials as reinforcement (see below, point 2 b).
2) Inhibiting the migration of dislocations by incorporating obstacles. Here, there are two possibilities for actually existing polycrystalline materials:
   (a) Inhibiting translation, that is, slippage, for example, by:
      (i) **Cold forming.** The dislocations that occur and migrate during forming are seen to pile up with increasing deformation level as forming progresses; as a consequence, they block each other and ultimately are no longer capable of slippage (Lomer–Cottrell dislocations). The probability of work hardening increases with the number of slip planes in the crystal lattice. Other dislocations migrate to the grain boundary, where they are stopped and cause subsequent dislocations to pile up. This means that the probability of work hardening increases as the grain size of the material is decreased.
      (ii) **Mixed crystal formation.** One type of atom dissolves in the matrix of the other and, depending upon the relative radii of the atoms, forms either an interstitial crystal or a substitution mixed crystal. Such lattice distortions result in a substantial increase in strength.
      (iii) **Transformation hardening (e.g., martensitic transformation).** Prerequisite for a martensitic transformation is an allotropic phase transformation, which the material passes through while cooling. Furthermore, the high-temperature modification must have a greater solubility for alloying elements than the low-temperature modification. During rapid cooling, the excess alloying element is forced to remain dissolved, leading to a pronounced lattice distortion which improves the strength and hardness.
   (b) Incorporation of multidimensional obstacles, such as:
      (i) **Grain boundaries (fine-grain hardening).** Slip planes end at grain boundaries, which is why grain boundaries represent an insurmountable obstacle for the migration of dislocations. The pile-up

of dislocations at grain boundaries results in the build-up of a strong counter-stress for the further migration of dislocations. The contribution of the grain boundaries to the hardening of the material increases as the grains of the material become finer (more boundary layers per unit volume) and the dislocation density falls off. The yield point (which is dependent on the dislocation density) is more strongly influenced by the grain size than by the tensile strength (Hall–Petch relationship).

(ii) **Precipitation (precipitation hardening).** This can be regarded as a continuation of mixed crystal formation. Here again, the different solubilities of atoms in host lattices at high and low temperatures are exploited. At high temperatures, alloys capable of precipitation hardening must consist entirely of mixed crystals. During slow cooling, due to the decreasing solubility with a drop in temperature for one type of atom or component, segregates precipitate out of the mixed crystal.

(iii) **Foreign particles by dispersion and fiber reinforcement.** The improvement in strength derives from the dispersed distribution of foreign particles or the incorporation of fibers in the material. The difference compared with precipitation hardening lies in the fact that the impurity particles do not dissolve in the matrix at high temperatures.

Until now, the strength properties discussed have referred to static loading. For dynamic loading (oscillatory or tumescent), as a result of material fatigue (see also Section 4.1.4), the materials show a fundamentally different behavior. Material fatigue can also result in rupture at load amplitudes below the static yield point. Due to the alternating tensile and compressive loading, dislocations already begin to migrate back and forth at low stress amplitudes. With prolonged cyclical loading, dislocations accumulate along the slip planes to slip bands, which become visible on the surface as intrusion or extrusion (Figure 5.6). The grooves arising from intrusion form crack nuclei – that is, starting points for the formation of cracks [4]. The incipient cracks continue to grow step-wise, and the residual cross-section ultimately fails as an overload breakage [5]. The introduction of compressive residual stresses in the regions of the material close to the surface can suppress the danger of crack formation and propagation.

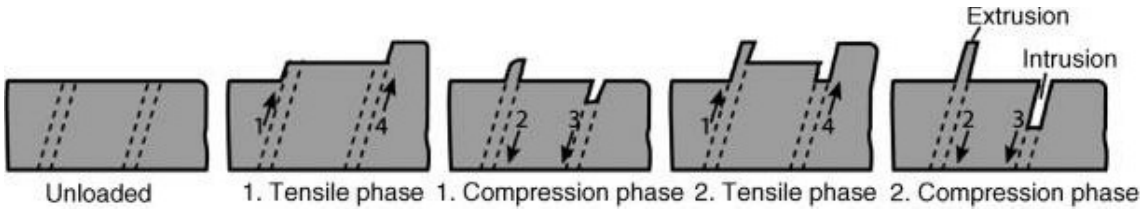


Figure 5.6 Formation of extrusions and intrusions (1...4: active slip planes) [4].

5.1.2
Influencing the Material Behavior at Higher Temperatures

The materials used in the construction of tools, machines, and systems are subjected to increasingly greater mechanical and thermal loadings. Whereas, purely mechanical loading can be taken into consideration via structural measures (by enlarging the load-bearing cross-section), at higher temperatures problems arise which can be solved only with the use of suitable materials. The general requirements for heat-resistant and high-temperature materials can be expressed in terms of the parameters high-temperature strength from the mechanical viewpoint, and high-temperature corrosion resistance from the chemical viewpoint. Decisive for the values of these parameters is the metallurgical load capacity of the material – that is, the extent to which a material suffers deterioration of the micro-structural properties over the specified service life at the given operating temperature. Here, above all it must be noted that thermally activated processes can destroy the micro-structural alterations introduced for the improvement of the strength (see Section 5.1.1). The thermally activated processes include:

- Diffusion
- Recovery, recrystallization and grain growth
- Creep and stress relaxation
- Thermo-mechanical fatigue.

5.1.2.1 **Diffusion**

Diffusion refers to material transport within solid, liquid, and gaseous matter, which occurs by the atomic exchange of positions of individual atoms. Diffusion is characterized by a macroscopic mass transport, which takes place as a result of the migration of individual atoms (in steps greater than one atom distance). Diffusion arises due to the presence of differences in concentration, giving rise to different enthalpies in the different regions of the system. Whilst the system strives to attain a thermodynamically more stable state, this requires an activation energy, in order for the atom to change its position. As a rule, this energy is introduced in the form of thermal energy, which causes the atoms to oscillate about their given positions. The lowest energy is required for diffusion via vacancies, so that here the highest probability exists. Moreover, the vacancy concentration c_L in the crystal lattice increases with temperature, because – due to the work of expansion with the introduction of heat – atoms are transported out of the volume to the surface, leaving vacancies behind. A detailed thermodynamic description of the formation of vacancies is provided in Ref. [3]. While the vacancy concentration at room temperature is approximately 10^{-12} (i.e., about one vacancy per mm^2), at the melting point the vacancy concentration rises to 10^{-4} (i.e., 100×10^6 vacancies per mm^2) [4]. The number of vacancies is calculated according to:

$$\text{Vacancy concentration } c_L: \qquad c_L = e^{-\frac{\Delta G_B^L}{R \cdot T}}$$

where

G_B^L = enthalpy of formation for vacancies
R = general gas constant (= 8.314 472 J K mol^{-1})
T = absolute temperature (K)

Here, it is possible to distinguish between three types of diffusion: volume diffusion (see also Section 6.1.4); grain boundary diffusion; and surface diffusion. As the packing density at grain boundaries is much lower than within the grains and the vacancy concentration and the degree of disorder are at the same time also greater, grain boundaries are always the preferred diffusion paths. Surface atoms have fewer neighboring atoms than atoms within the grain, so that surfaces possess higher energy potentials (surface energy); this favors the diffusion of atoms on the surface so as to obtain an energetically favorable position, with the goal of dissipating the maximum possible energy.

5.1.2.2 **Recovery, Recrystallization, and Grain Growth**

With the introduction of thermal energy, the alterations to the properties of plastically deformed materials take place in three stages: (i) recovery (ii) recrystallization; and (iii) grain growth. Due to plastic deformation, the energy content of the material is noticeably increased. Thermodynamically, this means that the micro-structural state is displaced in the direction of increasing nonequilibrium (higher potential). The stored energy is primarily comprised of the elastic distortion energy of the piled-up dislocations, the concentration of which rises from $10^{5\ldots6}$ mm mm^{-3} to $10^{8\ldots10}$ mm mm^{-3} during deformation. With sufficient activation energy (temperature rise), energy is dissipated by the healing and rearrangement of the lattice defects (recovery) or grain re-formation as a result of nucleation and grain growth (recrystallization). The number of energy-rich dislocations again falls off to the value of the nondeformed material, and at the same time the strength and hardness decrease [4]. The temperature at which the onset of recrystallization occurs depends upon the material; the higher the melting point T_S of the material, the higher the temperature for the onset of recrystallization. For many metals, the recrystallization temperature can be given as $T_R \approx 0.4 \times T_S$ (in K).

5.1.2.3 **Creep and Stress Relaxation**

At increased temperatures ($\sim 0.4 \times T_S$), in metallic materials under constant loading, a plastic deformation – described as "creep" – can occur below the yield strength R_e. The creep resistance is determined in an endurance test, in which a sample held at a constant temperature is subjected to a constant stress σ (mostly at constant loading, as this is easier to realize technically). The resulting change in shape ε is measured as a function of time and plotted in an $\varepsilon = f(t)$, (σ, T = constant) diagram (Figure 5.7). Creep takes place at different rates, allowing the division of the creep curve into three regions:

I. Transient creep (primary region): Deformation at a decreasing rate, due to the pile-up of dislocations blocking each other. Recovery processes simultaneously take place.

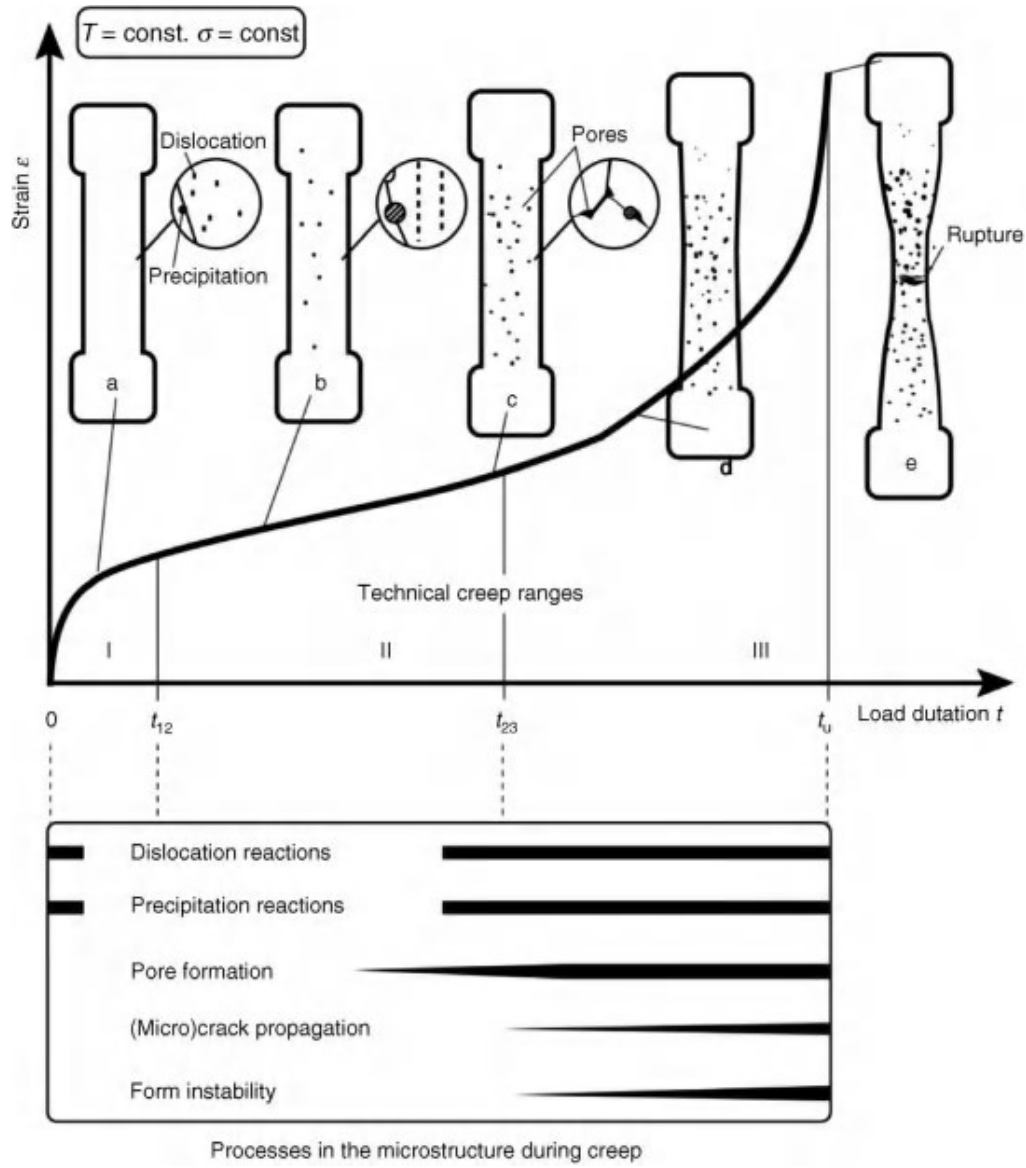


Figure 5.7 Creep curve and micro-structural alterations during endurance testing.

II. Stationary creep hardening and recovery processes are in equilibrium. The climbing of dislocations is the decisive process here. The thermal activation allows the circumvention of obstacles and nonmobile dislocations, so that creep continues to take place [4].

III. Accelerated creep (tertiary region): Deformation at an increasing creep rate, up to rupture of the sample. With increasing duration of loading, inter-crystalline processes, such as grain boundary slippage and grain boundary diffusion, predominate. Inter-crystalline creep fracture occurs as a result of the accumulation of creep damage to the microstructure, in particular as a result of micro-pores at the grain boundaries [5].

The information obtained from creep investigations does not always yield reliable guide values for the material behavior in practice. For example, it is often found that an applied load will change over time so that, if materials subject to creep loading are joined to materials which are only elastically deformed, stress relaxation will reduce the stress in both materials. Numerous examples of stress relaxation have been applied in engineering, including screw connections and pre-stressed concrete.

5.1.2.4 **High Temperature Strength**

High-temperature strength is the strength of a material at higher temperatures. To determine the heat strength of a material, it is not sufficient to determine the relevant parameters in tensile tests conducted at higher temperatures, and to use these as a basis for calculation. At higher temperatures, the specific strength properties of every material show a pronounced time dependence. The temperature limit, above which a noticeable time dependence is observed, roughly coincides with the recrystallization temperature. Moreover, the cyclic thermal stressing and mechanical stressing can cause fatigue. Due to thermal expansion, the crystal lattice grows and shrinks with cyclic thermal stressing, resulting in cyclic mechanical tensile and compressive stressing of the microstructure, and giving rise to the same phenomena as for isothermal cyclical mechanical loading. Whereas, for temperatures below the recrystallization temperature, the yield point at elevated temperatures is altogether sufficient, at higher operating temperatures the observation of the influence of time on the material behavior is indispensable. This includes all parameters determined in short-term and long-term testing, including:

- high-temperature yield strength and high-temperature tensile strength in tensile testing at elevated temperatures (short-term testing: thermal, static)
- creep strength in creep–rupture testing: creep resistance, creep limit, creep–rupture strength (long-term testing: thermal, static)
- high-temperature fatigue strength (thermal shock resistance) (short-term or long-term testing: thermal, dynamic).

The material behavior at elevated temperatures furnishes the basis for different methods of improving the high-temperature strength:

- **Increasing the melting point**: Alloying with metals having a high melting point and therefore a high recrystallization temperature (e.g., W, Mo, Ta, Nb), yielding mixed crystals which also have a high recrystallization limit.
- **Avoiding phase changes of allotropic materials**: From the standpoint of alloys, the high-temperature modification of different allotropic materials can be stabilized. A typical example of this is steel. Alloying with Ni, C, Co, Mn, and N stabilizes the austenitic face-centered cubic phase at room temperature. The lattice rearrangement in the ferritic body-centered cubic phase is suppressed, and the resultant lacking plasticity due to position exchange increases the creep stability. Furthermore, the face-centered cubic lattice possesses a higher packing density than the body-centered cubic lattice, inhibiting diffusion by the exchange of atomic positions.

- **Precipitation hardening**: The high-temperature strength can be influenced with alloys, by inducing highly temperature-stable precipitations. A typical example is the special carbides in steel, formed from alloying elements with a high affinity for carbon. This includes such refractory metals as Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, and W, as well as Co, Mn, and Ni, having high melting points. The stability of the phases increases with their complexity. Besides hard phases, intermetallic precipitations, such as the γ' phase Ni_3Al in super-alloys, are also utilized. With precipitation hardening for the improvement of high-temperature strength, three rules must be observed:
  - The type and distribution of the precipitation influence the magnitude of the creep resistance.
  - Due to the danger of embrittlement and inter-crystalline corrosion, precipitations at grain boundaries are to be avoided.
  - The hardening temperature must lie above the operating temperature, as otherwise over aging can set in.
- **Dispersion hardening**: This method of improving high-temperature strength is identical with the methods described for improving resistance at temperatures below the recrystallization temperature (Section 5.1.1)
- **Hot-cold forming**: Hot-cold forming (also referred to as semi-hot forming) takes place at higher temperatures, though below the recrystallization temperature in the recovery region. The operating temperature must lie below the forming temperature, in order that no softening occurs due to recovery. The degree of deformation must be carefully calculated, as the recrystallization temperature falls off with increasing deformation.
- **Diminishing the grain boundary**: A different behavior in terms of strength as a function of temperature is observed at the grain boundaries compared to inside the grains. While the strength of the grain boundary is greater at lower temperatures, at high temperatures the strength inside the grain is greater. For this reason, at lower temperatures the materials preferentially undergo trans-crystalline fracture within the grain, and at higher temperatures inter-crystalline fracture at the grain boundaries. The temperature at which the strength inside the grain and the strength of the grain boundary are identical is referred to as the "equicohesive temperature," attained in relation to the beginning of recrystallization. In order to avoid material failure at grain boundaries when used at high temperatures, directionally solidified alloys or single crystal alloys are employed.

5.2 Metallic Materials

The majority of the chemical elements are metallic in character. Due to the state of their atomic binding, metals possess good electrical conductivity, which decreases with increasing temperature, and a high thermal conductivity. For technical applications, alloys consisting of two or more elements are preferentially used, so as to allow the selective definition of physical, chemical, and mechanical

properties. With a current increasing demand for the weight reduction of materials, the proportion of lightweight metals used – especially of aluminum alloys, but also of magnesium and titanium alloys – is increasing. In tribological applications, copper materials are also important. Although, in the machinery sector, iron-based materials such as steel and cast iron still occupy the largest proportion of metallic materials, for highly stressed tribological components, specialized hard alloys and super-alloys have been developed which, in addition to the basic iron materials, include cobalt- and nickel-based alloys. Here, particular importance is attached to the refractory metals, which – due to their high affinity for B, C, N and O and their high melting points – represent important alloying elements. Finally, intermetallics which can selectively contribute to improving the strength of alloys should also be mentioned. Because of their complex crystal structures, intermetallics possess special properties which make them increasingly interesting as structural materials.

5.2.1
Lightweight Metals

Lightweight metals are the group of nonferrous metals and their alloys with a density $\varrho \leq 4.51\,\mathrm{kg\,dm^{-3}}$ for the pure metal. Of technical interest here are aluminum, magnesium, titanium, and their alloys (see Table 5.2). Besides high-strength steels and compound materials, lightweight metals represent the most important group of materials for lightweight construction. Their applications occur principally in the area of transportation engineering (aviation/aerospace, automotive industries), although with the current increased interest in preserving resources, lightweight constructions are becoming increasingly important in all areas of machine and system engineering (Figure 5.8).

5.2.1.1 **Aluminum and Aluminum Alloys**

After steel, aluminum is today the most widely used metal and, in the group of lightweight metals, the most important [7]. Aluminum comprises approximately 8% of the Earth's crust and, after oxygen (ca. 49%) and silicon (ca. 23.5%), is the third most common element; it is, therefore, the most widely represented metal, before

Table 5.2 Physical and mechanical properties of lightweight metals and iron.

	Symbol	Crystal structure	Density ϱ (g cm^{-3})	Melting point T_S (°C)	Youngs modulus (MPa)
Aluminum	Al	fcc	2.70	660.5	70 000
Magnesium	Mg	hcp	1.74	648.8	44 100
Titanium	Ti	hcp > 882 °C bcc	4.51	1660	110 000
Iron	Fe	bcc; > 911 °C fcc > 1392 °C bcc	7.87	1535	210 000

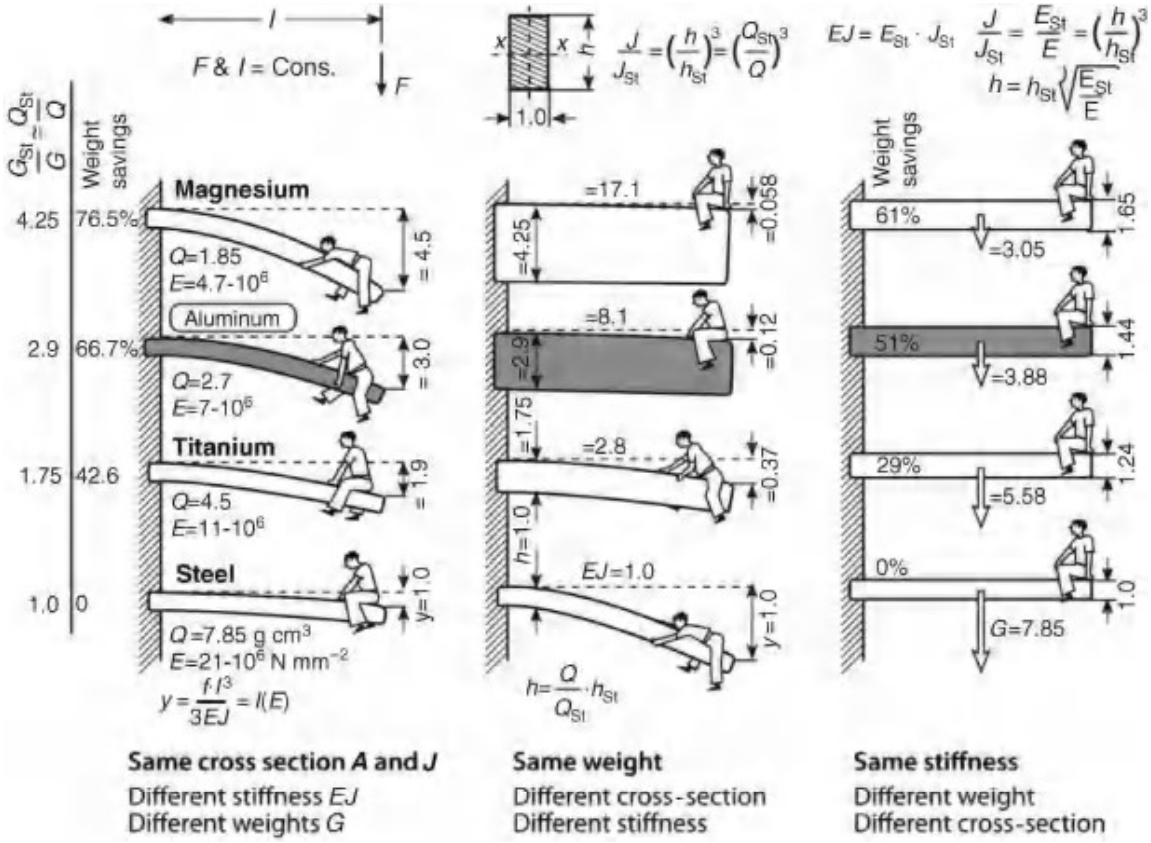


Figure 5.8 Comparison of the mechanical properties of aluminum, magnesium and titanium with those of steel [6].

iron (ca. 5%), magnesium (ca. 2%) and copper (ca. 0.01%). Due to its high affinity for other elements (particularly oxygen), aluminum is not found in pure form in nature. Primary aluminum is extracted as an intermediate product largely from bauxite, by way of γ-Al_2O_3 (clay). Al_2O_3 belongs to the most stable chemical compounds, and its reduction to metal requires a very high expenditure of energy [4]. Only with the development of dynamos (Werner von Siemens, in 1867) was sufficient electrical energy made available for the production of aluminum by electrolysis. Once extracted, aluminum can be recycled without problem; for the extraction of secondary aluminum, only 5% of this energy is required, permitting high recycling rates of 75–95% in Germany.

Conversely, however, the high affinity for oxygen also means that immediately stable protective oxide layers form (passivation) on metallic aluminum when it is exposed to the atmosphere. The oxide layers of aluminum are very dense, and therefore serve as good diffusion barriers; moreover, as the layers are not electrically conductive, this enhances their resistance to corrosion. Indeed, these layers are responsible for the very high corrosion resistance of aluminum in the atmosphere and in weak acids, although they rapidly dissolve in basic media. An additional improvement of the protective effect is achieved through the converting process (see

also Section 6.2.1). From a technical point of view, the most important properties of aluminum are its [8]:

- favorable ratio of strength to density;
- corrosion resistance in relation to the atmosphere and weak acids;
- favorable ratio of electrical and thermal conductivity to density; and
- good formability, due to its face-centered cubic structure.

The properties of aluminum can be influenced over a wide range by alloying with other elements. The following description of the influence of the main alloying elements Mg, Si, Cu, Zn and Mn is taken from Ref. [9]. Aluminum alloys can be divided into "wrought alloys" and "cast alloys," as well as hardenable and nonhardenable naturally hard alloys. The improvement in strength is the result of mixed crystal formation and strain hardening. For hardened Al alloys, a greater strength can be obtained by the precipitation of intermetallic phases (Al_2Cu, Mg_2Si, $MgZn_2$). Typical particle diameters for hardenable Al alloys are approximately 1 nm, while typical particle spacings are 10–20 nm; consequently, in a 1 mm^3 sample of alloy there are between 10^{10} and 10^{20} such particles [4]. Hardening takes place by solution annealing (e.g., 520 °C for AlMgSi), quenching and, finally, by natural aging or hot aging (e.g., 125–175 °C for AlMgSi).

Magnesium: With an increasing magnesium content, the elastic limit σ_P and the tensile strength R_m increase, while the elongation at fracture decreases by around 3 wt% Mg, but then increases again slightly. AlMg alloys are not brittle at low temperatures; only a few weight-percent of Mg renders aluminum stable against seawater and thus suitable for shipbuilding. Magnesium is also used for both wrought alloys and cast alloys.

Silicon: Silicon increases the flowability of the melts and lowers the melting point of aluminum cast alloys, causing a decisive improvement in both castability and mold-filling capacity. Silicon also helps to prevent shrinkage during solidification.

Copper: Copper improves the strength of aluminum, but also lowers the corrosion resistance due to its large electrochemical potential difference from aluminum. Copper is used for both wrought alloys and cast alloys; in the latter case it helps to reduce shrinkage during solidification.

Zinc: As an alloying element, zinc alone has virtually no influence on the strength properties. However, when combined with other elements, such as magnesium and copper, zinc achieves the highest strength properties compared with other alloy systems. The danger of a lack of corrosion resistance can be compensated by heat treatment. In cast alloys, zinc improves both the flowability and mold-filling capacity.

Manganese: Manganese improves the shaping behavior and, within limits, also the strength. The addition of manganese is limited to 1.5 wt% for wrought alloys, as brittle Al_6Mn phases would otherwise cause problems with further processing.

5.2.1.1.1 **Aluminum Wrought Alloys** Al wrought alloys are processed by rollers, extruding machines, pulling and forging to semi-finished products. Delivery is in the form of strand casting formats to finishing plants [7] for further processing, to profiles, films, sheets, and tubes. Identification is standardized in accordance with

Table 5.3 Classification of aluminum wrought alloys according to alloy series after DIN EN 573, identified with the specification EN AW.

	Series	Alloying elements		Groups	Applications
Naturally hard	1xxx	>99% Al		Al	Films, packaging, electronics
	3xxx	Mn	Mg, Cu	AlMn	Tubing, containers, heat exchangers
	4xxx	Si	Mg, Bi, Fe, CuNi	AlSi	Forge pistons, welding filler materials
	5xxx	Mg	Mn, Cr, Zr	AlMg(Mn)	Preformed car body parts, vessels
	8xxx		Fe, FeSi, FeSiCu	Special alloy	
Hardenable	2xxx	Cu	Mg, Mn, Bi, Pb, Si	AlCuMg	Screws, injection molds, gearwheels
	6xxx	MgSi	Mn, Cu, Pb	AlMgSi	Profiles, tubing, forged vehicle parts
	7xxx	Zn	Mg, Cu, Ag, Zr	AlZnMg(Cu)	Vehicle construction (steering/braking parts)

DIN EN 573, with the specification EN AW (W = wrought alloys) and a four-digit code number, divided into eight alloy series corresponding to the most frequently used alloying elements (Table 5.3). The alloys of the 6000 series are the most frequently used hardenable aluminum alloys [7]. Because of their comparatively high melting points, together with their high strengths, aluminum wrought alloys are particularly favored for aviation and automotive constructions and also in general machine construction, as they are comparatively well-suited for welding (see Figure 5.9).

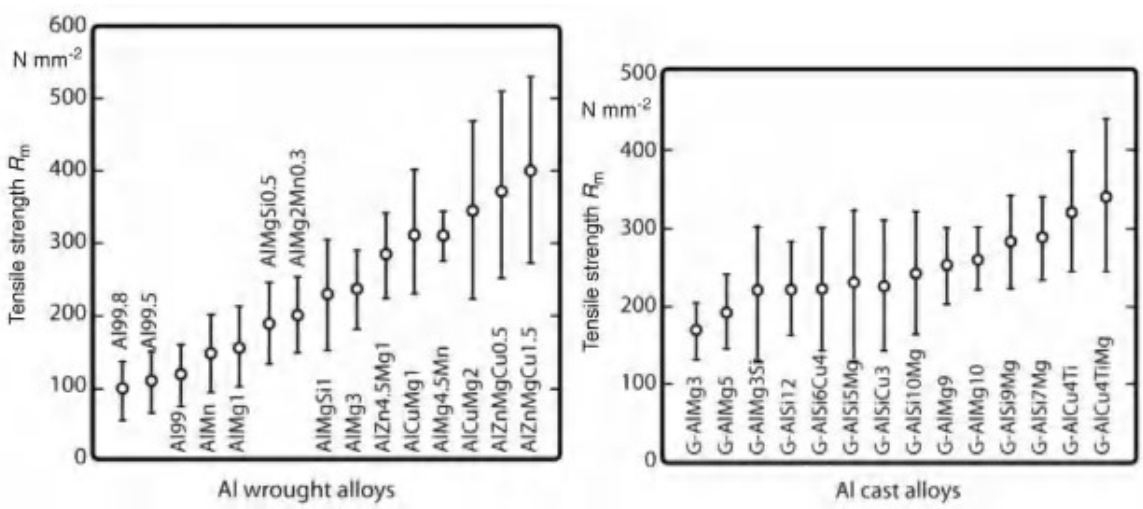


Figure 5.9 Comparison of the tensile strength ranges for important aluminum alloys.

Table 5.4 Classification of aluminum cast alloys with silicon as main alloying element in accordance with DIN EN 1706, identified with the specification EN AC.

Series	Alloying elements		Examples	Applications
	>99% Al		Al	
41xxx	Si	Mg, Ti		
42xxx	7% Si	Mg	AlSi7Mg	Engine housings, gearbox covers, wheel rims
43xxx	10% Si	Mg	AlSi10Mg	Engine and machine construction
44xxx	Si		AlSi	Complex thin-walled cast parts
45xxx	5% Si	Cu	AlSi5Cu	Engine blocks
46xxx	9% Si	Cu	AlSi9Cu	Motor and gearbox housings
47xxx	Si	Cu	AlSiCu	Cylinder heads
48xxx	Si	Cu, Ni, Mg	AlSiCuMgNi	Pistons for combustion engines

5.2.1.1.2 **Aluminum Cast Alloys** Al cast alloys are processed by sand casting, ingot mold casting and die casting, with 50% allocated to diecasting. Typical areas of application are engine blocks and other components for the automotive industry (see Figure 5.9) [7]. Cast alloys are identified by the specification EN AC (C = cast alloy), in accordance with DIN 1706, followed by a five-digit code. By far the greatest part of Al cast alloys are based on the binary system Al–Si with 2–20 w% Si. A detailed listing of the second digit is provided in Table 5.4.

5.2.1.2 Magnesium and Magnesium Alloys

Magnesium is not found in pure form in nature, but as compounds with other elements. The most important ore minerals for the extraction of magnesium are magnesite ($MgCO_3$) and dolomite ($MgCO_3 \cdot CaCO_3$). Magnesium also occurs in large amounts in seawater, to the extent of 1.3 kg m^{-3}. Although a small amount of pure magnesium was produced as early as 1808 by Sir Humphrey Davy, its industrial production did not begin until 1886, with the electrolysis of molten carnallite ($MgCl_2 \cdot KCl \cdot 6\ H_2O$). Today, there are two main processes for the production of magnesium:

$$\text{Electrolysis of molten magnesium chloride (75\%)}: \quad MgCl_2 \rightarrow Mg + Cl_2$$
$$\text{Silico-thermal process (25\%)}: \quad 2\,MgO + Si \rightarrow 2\,Mg + SiO_2$$

Magnesium is a good example of how materials and their applications can be influenced over the course of time by the re-evaluation and re-valuation of its properties and how these, in turn, have "compelled" further technological developments. In the aviation and automotive industries, magnesium was used as early as the 1930s. In the case of the Volkswagen "Beetle," the serial production of which began in 1939 and continued until 1962, more than 17 kg of magnesium alloys were processed per car when producing the gearbox and crankcase housings, generator arm, camshaft timing gear, bearing pedestals, and various covers. This amounted to a saving in weight of more than 50 kg compared to the use of steel [10]. Unfortunately, magnesium was subsequently driven from the market due to several disadvantages

which included poor strength, inadequate heat resistance, insufficient corrosion resistance, poor forging and cold-forming capabilities, higher costs and, allegedly, the danger of fire in its molten form and with the machining of aluminum. Nevertheless, lightweight construction technologies are today in great demand with regards to reducing the fuel consumption of automobiles. The corrosion resistance of magnesium alloys has been considerably improved with the use of so-called "high-purity" (HP) alloys, while environmental aspects have also been considered with modern production technologies utilizing water as a clean source of energy and permitting a good recycling capability. Another area worthy of mention here is the electronics industry, with the rapidly increasing demand for mobile telephones, laptops and digital cameras, all of which require lightweight housings (mostly made from magnesium alloys) [11].

Magnesium is a relatively soft, very non-noble metal, the glossy silver surface of which quickly oxidizes in air to create a dull finish. At temperatures up to 225 °C the shaping of magnesium is very difficult, as the metal – with its hexagonal, close-packed structure – crystallizes out, and deformation is possible only by base slipping and pyramidal twinning. The suitability for forming is improved enormously at temperatures above 225 °C, since above this temperature other slippage systems are activated. The major advantage of magnesium alloys is that they have the lowest density of all metallic construction materials, of the order of 1.74 g cm^{-3}, together with a high specific strength. The good castability, low energy requirements for melting, and the possibility of using steel forms leads to a reduction in the costs of manufacture. Unfortunately, the pronounced tendency of magnesium to oxidize requires the alloys to be cast under a shrouded gas atmosphere, which must be maintained throughout the entire casting process.

Magnesium alloys are distinguished by their, in part, outstanding processability and machinability. They are also suited to the manufacture of complex die-casting parts, and can also be machined and welded, albeit under a shroud gas.

Besides its poor cold-forming capability, other negative properties of pure magnesium which must be mentioned are its poor corrosion resistance, low strength, and pronounced shrinkage of 4% during solidification. To these can be added the relatively high thermal expansion coefficient, which is approximately 10% greater than that of aluminum. Consequently, there is a need to improve the properties of magnesium by alloying with different elements (Table 5.5). The most important alloying element is aluminum, which increases the tensile strength and hardness of the magnesium alloy, whereby the improvement in hardness is attributable to mixed crystal formation and the precipitation of intermetallic phases. The improvement in strength is, however, stable only up to a maximum temperature of 120 °C, as the mixed crystals again dissolve at higher temperatures. Aluminum improves not only the mechanical properties, but also to a large extent, the castability. For this reason, all magnesium alloys utilized on a large scale contain a not-insignificant amount of aluminum (3–9 wt%). A disadvantage here, however, is the increased tendency to micro-porosity.

The worldwide nomenclature for magnesium and magnesium alloys is in accordance with the ASTM (B 275) system. In this case, the first two letters describe the most

Table 5.5 Properties of certain alloying elements [12].

Properties	Alloying element
Strength	Al, Li, Mn, rare earths, Th, Zn
Hardness	Al, Si
High-temperature strength	Ag (with addition of rare earths), Ag (with additional Th, without Al, Mn), Ce
Elongation, ductility, shaping capability	Li, Zr, In
Creep strength	Ag (only with addition of rare earths), Ca, rare earths, Si, Th, also Y with Zr
Grain refinement, finer microstructures	Ca, Mn, Zn Zr, Ce, Y, Nd, Si, Zr, rare earths
Suitability for welding	Mn
Modulus of elasticity	Si, Be
Castability	Al, Zn
Reducing oxidation of the melt	Be
Reducing shrinkage during solidification	Sr
Corrosion resistance	
- Surface passivation	Al, Be, Si, Ge, Ga, P, Th
- Volume	Mn, Ga, Zn, Ca, V, Ti, Zr

frequently employed alloying element, in decreasing sequence; this is followed by numbers specifying the (rounded) percentage contents of the two alloying elements:

A	Aluminum	E	Rare earths
H	Thorium	K	Zirconium
M	Manganese	Q	Silver
S	Silicon	T	Tin
Z	Zinc	L	Lithium

An example of a commonly found magnesium alloy is AZ91; that is, a magnesium alloy with ca. 9% aluminum and ca. 1% zinc, with the DIN designation MgAl9Zn1. Other additional elements for MgAl alloys are principally zinc and manganese. Aluminum-free alloys are special alloys, mostly for use at higher temperatures, above 200 °C, and contain alloying elements such as zirconium, rare earths, thorium, and silver. Newly developed high-purity and corrosion-resistant magnesium alloys are identified with the additional specification, HP.

As with aluminum alloys, a distinction can be made between wrought alloys and cast alloys.

5.2.1.2.1 **Magnesium Cast Alloys** Magnesium cast alloys are predominantly processed in die casting. Important alloy groups are:

- magnesium–aluminum–zinc alloys: AZ91
- magnesium–aluminum–manganese alloys: AM20, AM50, AM60
- magnesium–aluminum–silicon alloys: AS21, AS41

- magnesium–aluminum–rare earth alloys: AE42
- magnesium–rare earth–silver–zirconium alloys: EQ21.

5.2.1.2.2 **Magnesium Wrought Alloys** The processing of magnesium wrought alloys takes place largely by forging and rolling. Due to the hexagonal close-packed structure, forming is made difficult. Cold forming leads to cracking, so that hot forming at temperatures above 350 °C is employed. Important alloy groups for wrought alloys include:

- magnesium–aluminum–zinc alloys: AZ31, AZ61, AZ80
- magnesium–zinc–zirconium alloys: ZK30, ZK40, ZK 60.

5.2.1.3 Titanium and Titanium Alloys

The fraction of titanium in the Earth's crust is around 0.6%, with the metal occurring in almost all minerals, soils and stones, in small amounts. Ilmenite ($FeTiO_3$) and rutile (TiO_2) are important for the extraction of titanium. The normal technical production processes for metallic titanium begin with liquid titanium halogenides (normally $TiCl_4$), as until now no economically feasible process for the direct reduction of titanium dioxide has been determined. The two most important production processes for titanium are the Kroll process (reduction with magnesium), and reduction with sodium. When these (relatively common) processes are used to produce high-purity titanium, the metal will be present as so-called "sponge titanium." Since even very small amounts of impurities, such as oxygen (>2%), iron (>0.3%), hydrogen, nitrogen and carbon can have a negative influence on the metal's properties (notably toughness and strength), the sponge titanium is re-melted in a high-vacuum furnace. Due to requirements in respect of purity, the method used involves the melting of consumable titanium electrodes, during which the titanium electrodes from the first re-melting process are consumed. Currently, all common titanium alloys are produced via melt-metallurgical processes.

In air, titanium forms an extremely stable protective oxide layer (passivation), rendering it corrosion-resistant in aqueous media over virtually the entire pH range, from 0 to 14. One remarkable property of titanium is its high strength with a relatively low density. Because of the high melting point ($T_{S,\text{Titanium}} = 1660\,°C$), titanium can also be used at higher temperatures, although above a temperature of 400 °C the strength properties fall off dramatically. As a result of the absorption of oxygen, nitrogen and hydrogen at higher temperatures, with titanium there is also the danger of embrittlement. Nonetheless, a strength comparable to that of high-tensile steels, a weight of only 60% of the steels, and an excellent corrosion resistance to many widely differing materials, have led to titanium materials becoming a permanent part of transport technology. A good example is that of aerospace technology; typically, 7% of the Airbus A330/A340 aircraft is produced from this class of materials, while in the aircraft engine the fraction is still higher, with about one-third of the materials used composed of titanium and its alloys. The landing gear of a present-day Boeing 777 is comprised almost entirely of titanium, with a saving in weight of 270 kg per aircraft compared to the steel that is normally used. Titanium is also well known for its outstanding *biocompatibility*, and is frequently used as an implant material, for

example in hip or knee joints. In the latter situation, the favorable ratio of weight to strength is also very beneficial.

Titanium and its alloys possess two micro-structural modifications. At room temperature, the hexagonal α-modification exists, which has only moderate cold-forming capability. However, at 882 °C a phase change to the high-temperature body-centered cubic structure (β-modification) occurs. The alloying of pure titanium with α- or β-stabilizing elements allows the displacement of this micro-structural transformation temperature in both directions. Sn and Zr show good solubility in both phases.

α-Stabilizers: As α-stabilizers, aluminum, oxygen, nitrogen and carbon extend the α-phase region to higher temperatures. In addition, a two-phase α-β-region forms [13]. The most important alloying element is aluminum, which in α-titanium alloys is limited to 6 wt% in order to prevent the precipitation of brittle intermetallic α_2-phases (Ti_3Al). Due to its hexagonal closed-pack structure, the α-titanium alloys are less ductile, and therefore have a poorer forming behavior. At the same time, however, the diffusion coefficient of the α-phase is two orders of magnitude lower than that of the β-phase, as a result of which the resistance to creep and oxidation is greatly increased. α-Titanium alloys are therefore preferentially employed for high-temperature applications, such as in jet engines. While Si, Sn, Zr and interstitially dissolved oxygen harden the α-phase, the Si atoms tend to cause segregations at dislocations and thus effectively prevent climbing, which leads to an improved creep behavior [13]. The 9 wt% limit for the aluminum equivalent applies also to the composition of α-titanium alloys:

$$\text{Al equivalent} = \text{weight\% Al} + 1/3\ \text{weight\% Sn} + 1/6\ \text{weight\% Zr}$$
$$+ 10\ \text{weight\% O} < 9\ \text{weight\%}$$

β-Stabilizers: Vanadium, iron, chromium, molybdenum and nobium, amongst others, stabilize the β-phase down to room temperature. The most important example of this group of materials is the alloy TiV15Cr3Al3Sn3. β-Titanium materials possess good hardening and cold-forming properties, although when compared with α-titanium materials they have a lower heat resistance and a greater tendency towards creep at higher working temperatures. The good cold-forming behavior can be attributed to the body-centered cubic crystal structure.

The alloying of pure titanium with simultaneously α- and β-stabilizing elements led to the production of titanium materials having both micro-structural modifications at room temperature, while combining the advantageous physical properties of both modifications, such as the outstanding combination of strength and ductility, in a single material (Table 5.6). The most important example of these so-called α-β-alloys is the alloy TiAl6V4, which – with approximately 50% of the market share – is also the most widely used titanium material. Due to the decreasing solubility of vanadium in the α-mixed crystal with falling temperature, TiAl6V4 can be hardened. Its broad spectrum of applications lies in the areas of aviation and aerospace technology, as well as in components subjected to heavy loading. The values of strength and toughness locate between those of steels and aluminum alloys, while the α-β transformation temperature of this material is 960–980 °C.

Table 5.6 Properties of selected titanium alloys.

Lattice structure	α-Ti alloys hcp	α-β-Ti alloys hcp + bcc	β-Ti alloys bcc
Properties	• Stable up to ~550 °C • Limited hardening capability • Poor cold-forming behavior • Low strength • High high-temperature strength • Low creep tendency • High oxidation resistance	• Stable up to ~430 °C • Good hardening capability • Good cold-forming behavior • Moderate strength • Moderate high-temperature strength • Moderate creep tendency • Good oxidation resistance	• Stable up to ~320 °C • Very good hardening capability • Very good cold-forming behavior • High strength • Low high-temperature strength • High creep tendency • Moderate oxidation resistance
Examples	• TiAl5Sn2,5 • TiAl7Zr12 • TiAl6Sn2Zr4Mo2Si0,1 • TiAl6Zr5Mo0,5Si0,2	• TiAl6V4 • TiAl6V6Sn2 • TiAl4Mo3V1 • TiAl6Sn2Zr4Mo6	• TiV15Cr3Al3Sn3 • TiV10Fe2Al3 • TiMo11,5Zr6Sn4,5 • TiAl3V8Cr6Mo4Zr4

A number of technical possibilities are employed for the hardening of titanium alloys:

- Intermetallic phases can be precipitated from the β-phase by quenching, followed by annealing. Here, the cubic body-centered β-mixed crystal is transformed to an hexagonal close-packed α-mixed crystal. The lattice shearing results in improved hardening, similar to the hardening of steel by martensite formation. Follow-on annealing causes a precipitation of the coherent β-phase from the newly formed α-phase, further improving the strength. The formation of a brittle transitional phase, the so-called ω-phase, must be avoided by the selection of a suitable annealing temperature.
- For alloys having β-stabilizing additives, with solution annealing and quenching, followed by aging, besides the α-phase the super-cooled metastable β-phase can also form, which during aging then passes through a metastable intermediate ω-phase to the α-phase and is transformed to a β-phase by enriching with additives.

5.2.2
Copper and Copper Alloys

Copper was the first metal to be exploited by mankind. Due to its face-centered cubic structure, copper possesses favorable prerequisites for plastic deformation [4]. The most important technical properties of copper include its high thermal and electrical conductivity, good castability behavior, and good chemical stability. Copper is principally extracted from its sulfide ores (chalcopyrite $CuFeS_2$, digenite CuS_2);

Table 5.7 Comparison of the physical and mechanical properties of copper and iron.

	Symbol	Crystal structure	Density ϱ (g cm^{-3})	Melting point T_S (°C)	Modulus of elasticity (MPa)
Copper	Cu	fcc	8.92	1083	125 000
Iron	Fe	bcc; > 911 °C fcc > 1392 °C bcc	7.87	1535	210 000

indeed, its noble character allows a simple extraction by oxidation of the sulfur in atmospheric oxygen, followed by cleaning in an air furnace or by aqueous electrolysis, with comparatively low energy requirements [14]. In spite of this easy extraction the price of copper is high, due mainly to its low natural occurrence (ca. 0.01%) in comparison with aluminum (ca. 8%) and iron (ca. 5%) (Table 5.7). Consequently, the recycling of copper materials is of major importance. The poor strength of copper led to its use as bronze for the manufacture of utensils as early as 2500 BC.

The strength of copper can be considerably enhanced by cold forming ($R_{m,annealed} = 180–230\ N\,mm^{-2}$ to $R_{m,hard\text{-}rolled} = 440\ N\,mm^{-2}$), although at the expense of a significant worsening of the ductility ($A_{annealed} = 40\%$ to $A_{hard\text{-}rolled} = 2\%$) [14]. With small amounts of alloying additives, mixed crystal hardening (Ag, As) or precipitation hardening (Cr, Zr, Cd, Fe, P, Be) can be achieved [4]. Because of copper's high thermal conductivity (the second highest of all metals after silver, and before aluminum), it is used as an ingot mold material in foundries. The thermal conductivity depends to a large extent on the purity of the copper. Hence, in order to reach a compromise between a high thermal conductivity and a moderate high-temperature strength, low-alloy copper materials with silver (e.g., CuAg0,1) or Be (e.g., CuBe2) as the alloying element are employed as ingot mold materials. The most technically interesting in this respect are the high-alloy binary copper alloys bronze (Cu with Sn, Al or Ni) and brass (Cu–Zn), along with the ternary alloys German silver (Cu–Zn–Ni), lead bronze (Cu–Pb–Sn), and red bronze (Cu–Sn–Zn) (Table 5.8).

5.2.3
Iron and Iron Alloys

Approximately 90% of the metallic materials used in machine construction are ferrous materials [14]. Iron, which comprises 5% of the structure of the Earth's crust, is extracted as iron ore (e.g., magnetite Fe_3O_4, hematite Fe_2O_3, or siderite $FeCO_3$), and reduced with carbon in a blast furnace to pig iron:

Energy supplied by the combustion of coal : $C + O_2 \rightarrow CO_2 + 394\ kJ$
Boudouard equilibrium : $C + CO_2 = 2\ CO$
Preliminary step (indirect reduction) : $Fe_3O_4 + CO \rightarrow 3\ FeO + CO_2$
Reduction process with carbon : $FeO + C \rightarrow Fe + CO$
$FeO + CO \rightarrow Fe + CO_2$

Table 5.8 Classification of copper alloys, properties and examples of their applications (all in wt%, summary taken from Refs [4, 8, 14]).

	Alloying element	Examples of applications
Sn bronze		Wear and chemical resistance increase with Sn content
(Cu–Sn)	1.5% Sn	Wrought alloy: "post bronze", overhead telephone lines
	6–8% Sn	Wrought alloy: "bronze wire", contact springs
	10–14% Sn	Cast alloy: worm gears, gearwheels, plain bearings, impellers
	20–25% Sn	Cast alloy: bells
Al bronze	3–10% Al	Hot steam fixtures, plain bearings, guides, rollers
(Cu–Al)		Resistant to seawater, sulfuric acid, saline solutions
	+ Fe, Mn, Ni, Si	For improvement of strength by precipitation hardening
Ni bronze	1–45% Ni	Heat-resistant pipes, coins, thermo-elements (CuNi44)
(Cu–Ni)		Very good corrosion resistance and high-temperature strength
	+ 1.5% Fe, 2% Mn	Improves corrosion resistance
	+ 0.15–1% Si	Improves heat resistance by precipitation of Ni_2Si
Brass	Up to 20% Zn	Red brass, very ductile, imitation gold leaf
(Cu–Zn)	20–37% Zn	Yellow brass, deep-drawing parts such as sleeves, musical instruments
	37–44% Zn	Hard brass ($\alpha + \beta'$)-alloy for screws, metal fittings
	+ 1–2% Pb	Improves machining capability of hard brass
Special brass	0.1–10%	Ship propellers, control elements, bearings, munition
(Cu–Zn + X)	additives	shells
	Al	Improves strength and resistance to corrosion and oxidation
	As, P	Improves corrosion resistance, suppresses elution of zinc
	P	Improves castability
	Mn, Fe	Improves sliding properties, serves for grain refining
	Ni	Improves corrosion resistance and high-temperature strength
	Sn, Si	Improves sliding properties and corrosion resistance
German silver	11–46% Zn	Eating utensils, medical instruments, keys
(Cu–Zn–Ni)	11–28% Ni	Good shaping behavior, corrosion-resistant
Pb bronze	5–18% Pb	High-stress plain bearing materials, e.g. for Diesel motors
(Cu–Pb–Sn)	4–10% Sn	Very high thermal conductivity, good dry-running properties
	+ Ni, Zn, Fe, Sb	Good resistance to dynamic and impact loading
Red bronze	3–10% Sn	Bearing sleeves, paper roll sleeves, fittings
(Cu–Sn–Zn)	2–7% Zn	Good corrosion resistance, good rollability

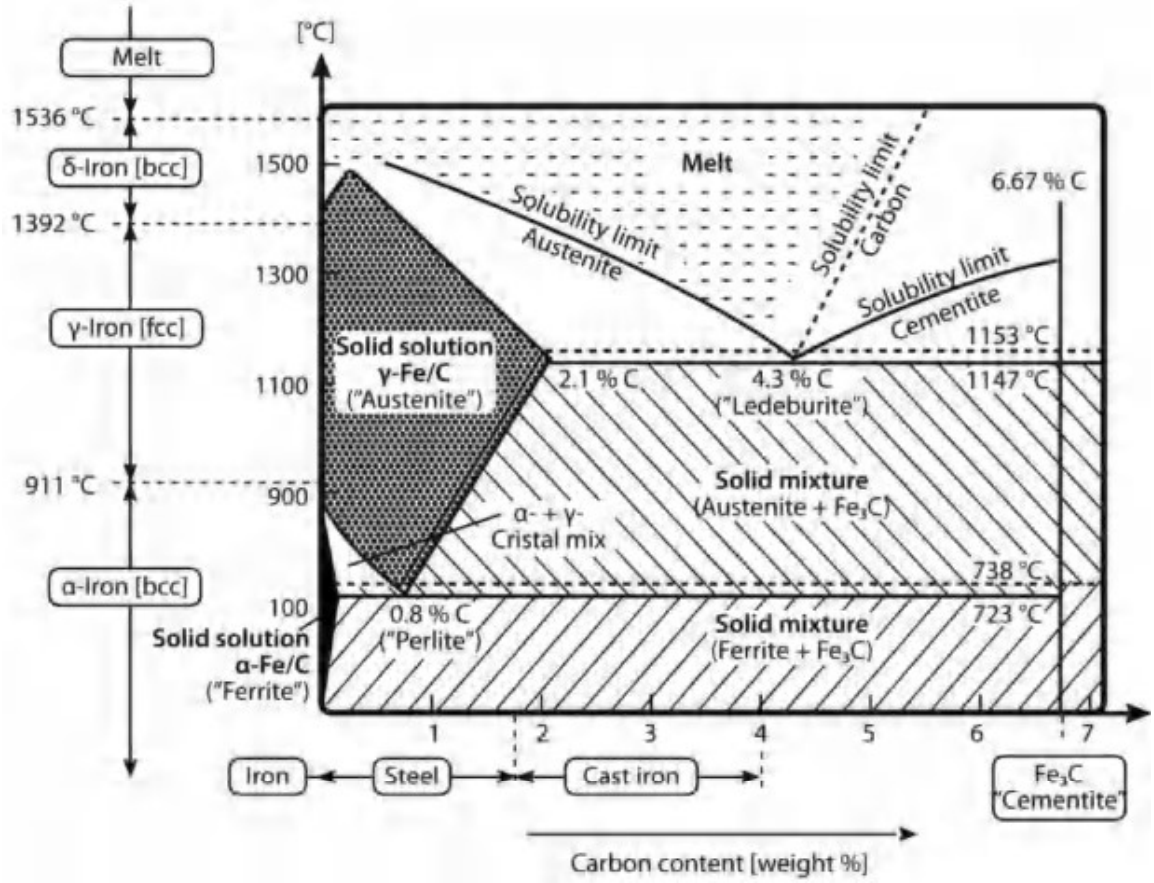


Figure 5.10 Fe–Fe_3C phase diagram.

The production costs and availability of iron are therefore relatively favorable today. The cubic crystal structure imparts a good plastic deformability with a high rigidity [15]. The superiority of iron-based alloys compared with other materials derives from their strength and toughness at low cost, while the high solubility of iron for many elements furnishes the basis for wide-ranging alloy concepts. The most important alloying constituent is the cost-effective element, carbon. The most technically important of these alloys is the meta-stable iron–cementite (Fe-Fe_3C) (see the phase diagram in Figure 5.10). Iron materials are classified as either *pure iron*, which contains only traces of other elements, *steel* (containing < 2.1 wt% C), and *cast iron* (containing $2.1 <$ wt% C < 4) (Table 5.9).

Table 5.9 Physical and mechanical properties of iron.

	Symbol	Crystal structure	Density ϱ (g cm^{-3})	Melting point T_S (°C)	Modulus of elasticity (MPa)
Iron	Fe	bcc; $>$ 911 °C fcc $>$ 1392 °C bcc	7.87	1535	210 000

The properties of iron materials are determined by the microstructure, which can be influenced by alloying, the manufacturing process employed, and heat treatment. Since, in Europe alone, more than 2000 types of steel are registered, only a general overview of the classification of iron materials can be provided here, though particular emphasis is applied to the alloying concepts.

5.2.3.1 **Cast Iron**

Cast iron refers to cast iron–carbon alloys incorporating 2.1–4 wt% C and, according to intended purpose, 0.5–3 wt% Si (Table 5.10). Cast iron possesses good corrosion resistance in relation to atmospheric air. Following solidification, it is possible to distinguish – according to the color of the fracture structure – between *white cast iron*, for which solidification takes place in accordance with the meta-stable system Fe–Fe_3C; and *gray cast iron*, for which solidification takes place in accordance with the stable iron–graphite system. In the case of white cast iron, the high fraction of cementite (Fe_3C) results in a high hardness and brittleness; white cast iron also demonstrates a low tensile strength, and a high compressive strength and wear

Table 5.10 Classification of cast iron.

White cast iron			**Gray cast iron with lamellar graphite GJL (formerly GG)**	**Gray cast iron with spheroidal graphite GJS (formerly GGG)**	**Special cast iron GLY**
Composition					
2.4–3.3% C 0.5–1.4% Si			3.0–3.5% C 1.5–2.5% Si	3.5–3.8% C $<$0.01% S slight addition of Mg	1.5–3.5% C High-alloy with Si, Mn, Cr, Ni, Al
C as Fe_3C (cementite)			C primarily as graphite	(a) pearlitic base mass with C as graphite and Fe_3C (b) ferritic base mass with C as graphite	
Identification					
White fracture structure			Gray fracture structure	Gray fracture structure	High-alloy
Hard cast GJN (formerly GH)	Malleable iron GJM (formerly GT)				
	white (GTW)[1]	black (GTS)[2]			

[1]GTW: Annealing in an oxidizing atmosphere decarburizes the peripheral zone → white fracture structure
[2]GTS: Annealing in a neutral atmosphere

resistance. Notably, hard cast iron (GJN) is used as the balls in ball-mills, as the crusher jaws in milling machines, and as mandrels for drawing pipes, drawing plates or rolling. It is also used as clear chilled casting with a white cast structure of the peripheral zone, with a gray cast structure as the core, for example, in a camshaft. With subsequent long-term annealing, the malleable iron (GJM) causes disintegration of the cementite. The relatively low Si content prevents the formation of lamellar graphite, while the temper carbon coagulates in the form of flakes. A large part of the carbon is incorporated into the microstructure of the gray cast iron as graphite. Although gray cast iron is brittle, due to the graphite inclusions it has a high damping capacity; the lubricating effect of the graphite also results in a good machining behavior of cast iron. At this point, it is possible to differentiate between gray cast iron with lamellar graphite (GJL) and spheroidal graphite (GJS), according to the form of graphite precipitation. Among the different types of cast iron available, gray cast iron with spheroidal graphite most closely approximates the steel construction material since, with its hot-shaping capabilities, it offers certain advantages over steel and malleable iron. For example, with suitable heat treatment and alloying, the base material can be hardened or quenched and tempered, which in turn provides an improvement of the mechanical parameters. With high contents of nickel, chromium and other alloying elements, specific properties such as high-temperature strength, sufficient toughness at low temperatures, high corrosion resistance to sulfuric and nitric acids, or scaling resistance can be adjusted (special cast iron). Hardness values of up to 65 HRC, with an elastic modulus comparable to that of steel, can be achieved. Consequently, special cast iron is suited for use in motor or aircraft engine construction, for example, in crankshafts, crankcases, connecting rods, or camshafts.

5.2.3.2 **Steel**

Steel is an iron–carbon alloy with up to 2.1 wt% C, and with hot-shaping capability. Above 2.1 wt% C, brittle cementite (Fe_3C) increasingly forms, leading to a loss of the forming capability. In addition to the carbon content, the rate of cooling during solidification from the melt has a very important influence on the resultant microstructure, which can be read from time–temperature transformation diagrams for given compositions. With slow cooling, the stable system corresponding to the iron–carbon diagram is formed, whereas with very slow cooling a complete martensite formation will occur.

Besides carbon, other alloying elements play an important role in the formation of the microstructure. These include (mainly) nickel and chromium and their equivalent alloying elements which stabilize the austenitic γ-phase ("Niccomann") and ferritic α-phase ("Craltitasimovw"). The relationship between the composition of the alloy and the formation of the microstructure is given by the Schaeffler diagram (Figure 5.11). High-alloy steels having both an austenitic and a ferritic phase are described as duplex steels. In contrast to austenite, the ferrite is ferromagnetic (up to 769 °C). Austenite also has a much greater tendency towards strain hardening and, overall, is far tougher than ferrite.

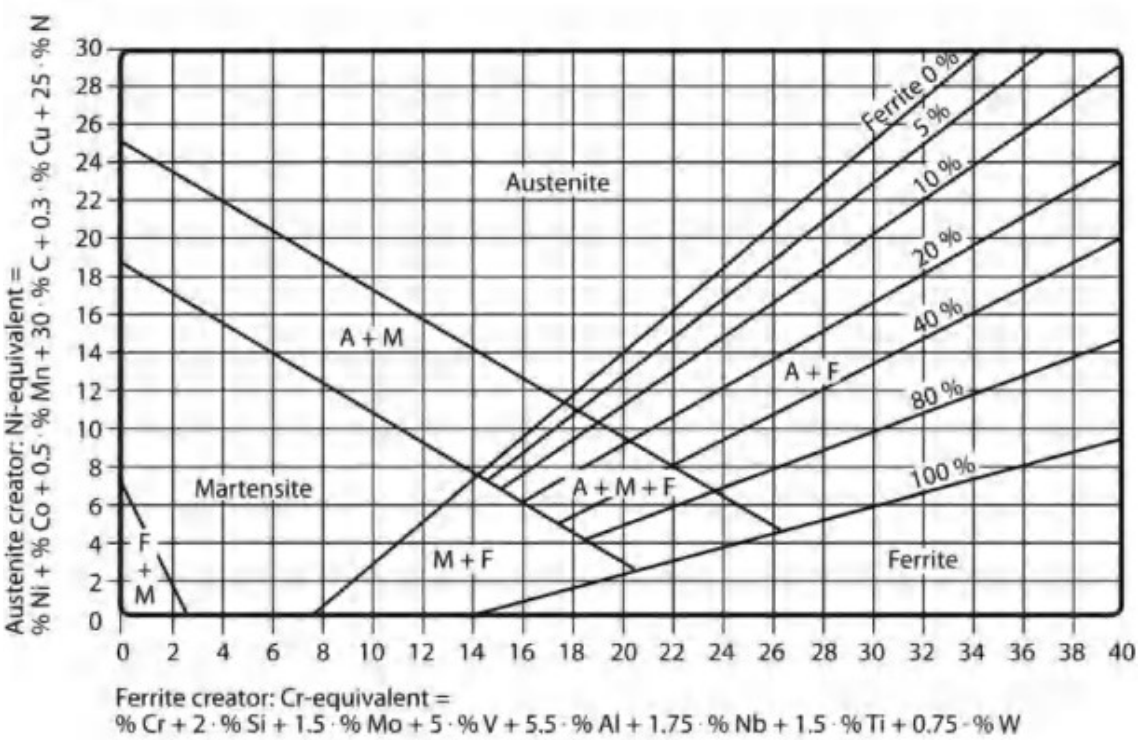


Figure 5.11 Microstructure diagram for steel (after Schaeffler).

The classification of steels is in accordance with DIN EN 10027-2 (1992), in conjunction with DIN EN 10020, in the form of a five-digit numbering 1.XXYY [16]. Here, the 1 refers to the main material group "steel", XX describes the steel group, and YY describes the identifying number within the steel group. A distinction is made between nonalloyed and alloyed steels, as well as between quality steels and high-grade steels (Table 5.11). High-grade steels are steel types which are intended for heat treatment and, because of their special manufacturing conditions, they are

Table 5.11 Classification of steels in accordance with DIN EN 10027-2, in conjunction with DIN EN 10020 [16].

Non-alloyed steels		Alloyed steels				
Quality steels	High-grade steels	Quality steels	High-grade steels			
			Tool steels	Different steels	Chemically resistant steels	Structural, machine construction and container steels
1.0009–1.0765	1.1004–1.1830	1.0800–1.0987	1.2002–1.2891	1.3202–1.3993	1.4000–1.4988	1.5015–1.8998

purer than quality steels. For practical reasons, alloyed steels are classified as low-alloy (total alloying elements <5%) and high-alloy (>5%). Low-alloy steels have essentially the same properties as nonalloyed steels [4], although as a result of the alloying elements they show much better hardening capability. Furthermore, the high-temperature strength (e.g., due to Mo) and tempering stability (e.g., due to carbide precipitation) can be increased [4]. A summary of the influence of the most important alloying elements on the properties of steel alloys is provided in Table 5.12.

Case-hardening steels: These are low-alloy or nonalloyed steels with a carbon content of <0.3 wt%, which have been specially developed for case hardening (see also Section 6.2.9.2). Higher carbon contents for these steels would lead to undesirable austenitization of the peripheral zone. In this case, the important alloying elements are Mn, Cr, Mo, and Ni. In particular, the hardening capability is improved by Cr and Mn additives, while Ni improves the core toughness and enhances the depth of hardening.

Nitrided steels (1.8504–1.8599): These are Cr–Mo quenched and tempered steels with additives of Al, V, and Ni. Mo improves the high-temperature strength and creep-rupture strength and reduces annealing embrittlement; Ni-alloyed steels are better suited to applications with larger cross-sections. The diffusion of nitrogen into the steel during the nitriding process (see also Section 6.2.9.3) vastly improves the edge hardness and the corrosion resistance for both low-alloy and nonalloyed steels.

Quenched and tempered steels: These are high-grade steels with high tensile strength and high endurance strength. Due to tempering, the martensite hardness obtained during hardening is in fact somewhat lowered, although the toughness is considerably improved. The tempering properties of nonalloyed steels can be attributed to the content of C and Mn, whereby increasing contents increase the yield point and tensile strength values. Although, with increasing Mn content, the through quenching and tempering is improved, a slightly coarse grain is formed, but this can be partly avoided by using very low-V content additives. An increased Si content enhances the hardness capability and tempering stability, as do higher Mn contents. A series of Cr-alloyed steels, in part with Mo, W and V, or Ni and Mo, has also been developed; these have a reduced tendency to embrittlement during annealing while, at the same time, their penetration hardening capability and through quenching and tempering are improved. In this case, the carbon content lies between 0.17 and 0.62 wt% and, with refractory metals, contributes to an improvement of the strength via the precipitation of special carbides.

Machining steels: These have been developed for efficient serial production on automated machine tools. The improved machinability is achieved mainly by the high S contents (0.18–0.30 wt%); this leads to the formation of brittle inclusions in the steel, at which the chip breaks away during machining. The addition of Pb has a similar effect, giving rise to finely distributed lead inclusions; however, for reasons of immission protection Pb is rarely used. In combination with Mn, soft, linear arrays of manganese sulfide inclusions form, thus improving the cutting speed. A slight increase in the content of P (up to 0.1 wt%) has a favorable influence on the possibility of obtaining smooth and glossy work piece surfaces.

Table 5.12 Influence of alloying elements on the properties of steel [17].

Alloying element	Mechanical properties																Magnetic properties				
	Hardness	Strength	Yield print	Elongation	Reduction of area	Impact value	Elasticity	High temp. stability	Cooling rate	Carbide formation	Wear resistance	Forgeability	Machinability	Scaling	Nitrability	Corrosion resistance	Hysteresis	Permeability	Coercive force	Resonance	Loss of watt
Silicon	↑	↑	↑↑	↓	~	↓	↑↑↑	↑	↓	↓	↓↓↓	↓	↓	↓	↓	–	↓↓	↑↑	↓↓	–	↓↓
Manganese at perlitic steels	↑	↑	↑	~	~	~	↑	~	↓	~		↑	↓	~	~	–					
Manganese at austenitic steels	↓↓↓	↑	↓	↑↑↑	~	–	–	–	↓↓	–	–	↓↓↓	↓↓↓	↓↓	–	–	not magnetic				
Chromium	↑↑	↑↑	↑↑	↓	↓	↓	↑	↑	↓↓↓	↑↑	↑	↓	–	↓↓↓	↑↑	↑↑↑			↑	↑↑	
Nickel at perlitic steels	↑	↑	↑	~	~	~	–	↑	↓↓	–	↓↓	↓	↓	↓	–	–			↑↑	↑↑	
Nickel at austenitic steels	↓↓	↑	↓	↑↑↑	↑↑	↑↑↑	–	↑↑↑	↓↓	–	–	↓↓↓	↓↓↓	↓↓	–	↑↑	not magnetic				
Aluminum	–	–	–	–	↓	↓	–	–	–	–	–	↓↓	–	↓↓	↑↑↑	–			↑↑	↑↑	
Tungsten	↑	↑	↑	↓	↓	~	–	↑↑↑	↓↓	↑↑	↑↑↑	↓↓	↓↓	↓↓	↑	–			↑↑↑	↑↑↑	
Vanadium	↑	↑	↑	~	~	↑	↑	↑↑	↓↓	↑↑↑↑	↑↑	↑	–	↓	↑	↑					
Cobalt	↑	↑	↑	↓	↓	↓	–	↑↑	↑↑	–	↑↑↑	↓	~	↓	–	–		↑↑	↑↑↑	↑↑↑	
Molybdenum	↑	↑	↑	↓	↓	↑	–	↑↑	↓↓	↑↑↑	↑↑	↓	↓	↑↑	↑↑	–			↑		
Copper	↑	↑	↑↑	~	~	~	–	↑	–	–	–	↓↓↓	~	~	–	↑					
Sulfur	–	–	–	↓	↓	↓	–	–	–	–	–	↓↓↓	↑↑↑	–	–	↓					
Phosphorus	↑	↑	↑	↓	↓	↓↓↓	–	–		–	–	↓	↑↑	–	–	–					

↑ Increase ↓ Reduction ~ Ca. constant – Not characteristic or unknown Several arrows = more intensive effect

Rolling bearing steels (1.3501–1.3576): These contain 0.77–1.2 wt% C, in addition to Cr and in part also Mo and V. Rolling bearing steels are generally through-hardened steels, although high-temperature strength and stainless steels are also employed. The best known – and, without doubt, the best investigated – rolling bearing steel is 100Cr6. Rolling bearing steels are particularly subject to very high tensile–compressive loading and wear attack during operation. Because of the very high local (mostly point shaped) load transmission, special demands are placed on rolling bearing steels; these include a high degree of purity, a uniform distribution of the alloying and micro-structural components, sufficient toughness and, at the same time, a high surface hardness. In practice, rolling bearing steels usually have a high-strength martensitic-carbidic microstructure. In order to obtain an optimal machinability, it is necessary for rolling bearing steels to produce uniformly grained carbides of medium size, without residual lamellar carbide (perlite), by soft annealing. For low-alloy case hardening steels, on the other hand, a microstructure with a uniformly distributed perlite is better suited.

Wear-resistant steels (1.3401–1.3433): The classical wear-resistant steel with high wear resistance and, at the same time, cold-hardening capability, is Mn hard steel (1.3401: X120Mn12). The highest wear resistance is obtained with alloys in which the C: Mn content is approximately 1: 10. For steel casting for high compressive loading, higher contents of Mn (up to 17 wt%) and chromium (up to 2.5 wt%) are chosen. For wear-resistant deposit welding, according to the wear requirements welding electrodes and rods of austenitic Cr–Ni–Mn steels are also used, besides those of Mn hard steel (e.g., in the welding of X15CrNiMn 18-8 rails with 6 wt% Mn). For wear resistance, a eutectoid microstructure is important; in this case, free ferrite is unfavorable, but free carbides are generally advantageous. For the same strength, a microstructure with a streaked perlite gives the highest wear resistance. However, with increasing strength the wear resistance is also increased, so that quenching and tempering is mostly advantageous.

Tool steels: These are classified, according to their application, into:

- Nonalloyed tool steels (1.1520–1.1830)
- Alloyed tool steels (1.2002–1.2891). These include tool steels for cold working, up to 200 °C working temperature; and tool steels for hot working, above 200 °C working temperature
- High-speed steels (1.3202–1.3397); these are used primarily for machining tools, but also for cutting and forming tools, with W, Mo, V and Co as the alloying elements. The high fraction of high-melting-point special carbides ensures a sufficient hardness when working at temperatures above 600 °C.

Stainless steels (1.4000–1.4690): These are high-alloy steels with <1.2 wt% C and >12 wt% Cr, which means that they can passivate. Austenitic Cr–Ni steels show a greater corrosion resistance. While Mo additionally improves the stability of the passive layer and thus lowers the susceptibility to pitting in media containing chlorides. Alloying with Cu improves the resistance to sulfuric acid. The addition of Ti and Ta/Nb binds carbon in the grain, preventing sensitization by chromium carbide ($Cr_{23}C_6$) precipitation; this must be prevented from occurring at the

grain boundaries due to the danger of inter-crystalline corrosion. When there is a danger of inter-crystalline corrosion, the C content should be simultaneously reduced to <0.03 wt%.

High-temperature strength steels (1.4901–1.4988): In order to achieve high-temperature strength and to be as stable as possible, these steels must possess a (preferentially austenitic) microstructure with high recovery and recrystallization temperatures. Precipitation hardening is achieved by the formation of special carbides, nitrides and intermetallic compounds, which allow cold or hot hardening by distending or forging, followed by annealing, above the working temperature. Up to working temperatures of about 600 °C, steels capable of quenching and tempering, with 12 wt% Cr and additives of Mo and V are employed. For higher temperature ranges or greater stressing, Cr–Ni steels distinguished by their good creep–rupture strength even above 600 °C are used. High-temperature steels have a relatively high Cr content of >12 wt%, and this results in a sufficient stability against scaling for normal requirements. In order to improve the creep–rupture strength, small amounts of Nb, Mo, and V are added. The temperature limit of these steels, which are frequently used in the construction of power plants, is about 750 °C.

Cast steels: These are Fe–C alloys with a C content of <2 wt%, with and without additional alloying elements. For parts not subjected to high stressing, a nonalloyed cast steel can be used in the normalized state. However, for higher demands such steels must be quenched and tempered, or a low-alloy cast steel should be chosen; these are also mostly normalized. For greater chemical or thermal stressing, rust-proof and acid-resistant alloy types and heat-resistant cast steels with high contents of Cr, Ni, Mo, and Si additives (and also occasionally Nb) are available.

5.2.4 Hard Alloys

Hard alloys are multiphase metallic materials manufactured in melt-metallurgical processes and further processed in different ways [18]. Their microstructure is comprised of a relatively tough matrix of the metals iron, cobalt, or nickel (Table 5.13), in which hard phases, such as carbides, borides and, in a few cases also silicides, are embedded [19, 20]. According to the matrix metals, it is possible to distinguish between three groups of hard alloys.

Iron, nickel, and cobalt are distinguished by sufficient solubility for the hard phase-forming elements in the melt, and low solubility in the solid state. As a result, during cooling of the melt, a precipitation of the hard phases takes place. The base metals also possess high melting points, and this results in the high-temperature resistance values of the hard alloys. In particular, Co-based alloys allow maximum working temperatures in excess of 700 °C. Some typical alloy concepts are listed in Table 5.14.

In combination with a metallic matrix with embedded hard phases, materials with a combination of high wear resistance and sufficient resistance to fracture can be obtained. The fraction of hard phases is generally in the range of 15–45 vol%, while

Table 5.13 Physical and mechanical properties of the base metals for hard alloys.

	Symbol	Crystal structure	Density ϱ (g cm^{-3})	Melting point T_S (°C)	Youngs modulus (MPa)
Iron	Fe	bcc; > 911 °C fcc > 1392 °C bcc	7.87	1535	210 000
Cobalt	Co	hcp > 417 °C fcc	8.89	1495	210 000
Nickel	Ni	fcc	8.91	1453	210 000

Table 5.14 Groups of hard alloys and examples of alloys.

Base metal	Alloying elements leading to hard phase formation		Other alloying elements
Fe	Cr, W, Mo, V, (Nb, Ti)	C, (B, Si)	Mn, Ni, (Co)
Co	Cr, W, Mo	C, (B, Si)	Ni, Cu, Fe
Ni	Cr, (Nb, Mo, W)	B, Si, (C)	Cu, Fe, (Co)
Base metal	**Composition**	**Description**	
Fe-based	FeCr12C2.1	X 210 Cr 12	Cold working steel
	FeCr5Mo1VC0.4	X 40 CrMoV 5 1	Hot working steel
	FeW6Mo5Cr5V3C1.3-P	HS 6-5-3	High-speed steel
Co-based	CoCr29W5C1.2	Stellite 6	Co–Cr–W matrix with M_7C_3
	CoCr20Mo20FeNiSiB2.5		Co–Cr–Mo matrix with M_3B_2
Ni-based	NiCr18Si4B3C		Ni–Cr–Si matrix with M_3B
	NiCr18Mo18Si4Nb3B4C		Ni–Cr–Si matrix with M_3B_2

materials with >50 vol % (hard compound materials, pseudo-alloys) are manufactured via powder-metallurgical processes. The volume fraction and composition of the matrix itself are decisive for the (heat) resistance and corrosion resistance. To a large extent, the precipitated hard phases determine the wear behavior. In this case, the important influential factors include the size, form, distribution, alignment, composition and volume fraction of the hard phase. The bonding between the hard phases and the matrix also has a major influence on the mechanical properties. Hard phases with a high fraction of metallic bonds (e.g., metal carbides) are preferred, as they form coherent or partly coherent precipitations from the metallic matrix.

During solidification of the hard alloy, primary (directly from the melt) and/or eutectic hard phases are precipitated. In the greatly simplified binary system (Figure 5.12), which consists of a matrix metal M and C, B or Si, during the solidification a sub-eutectic melt initially begins so as to form a primary metal matrix, which then grows into the melt in the form of dendrites. During further cooling, the metal cells formed in this way are surrounded by a eutectic system comprised of the metal matrix and the eutectic hard phases. In the case of super-eutectic alloys, coarser primary hard phases are initially precipitated out, but

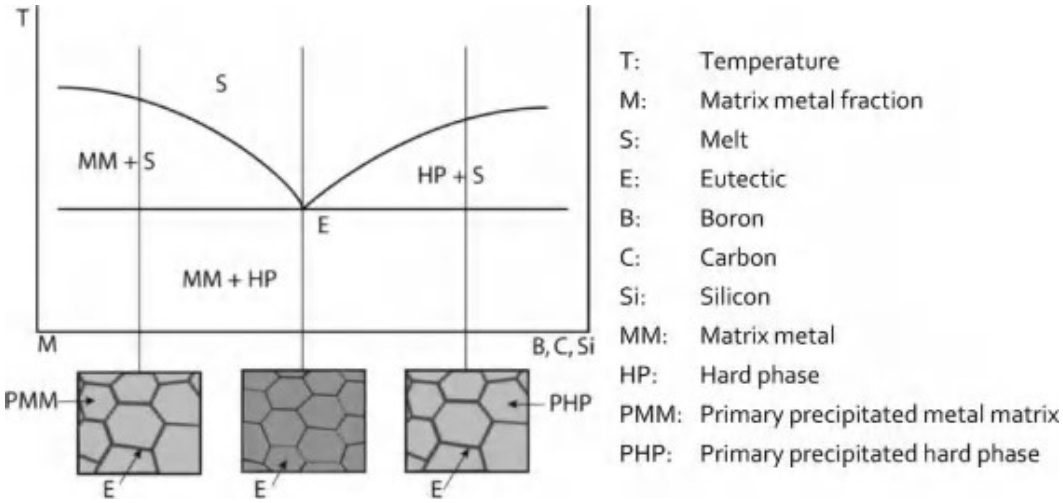


Figure 5.12 Schematic representation of the formation of hard alloy microstructures during solidification with a eutectic (after Ref. [20]).

during further cooling below the eutectic temperature, the eutectic will then form. Besides being precipitated from the melt, hard phases can form as a result of further cooling, or by heat treatment processes from the solidified mixed crystal. In this case, secondary hard phases are spoken of which, due to their size, are mostly allocated to the matrix [21]. In fact, they are considerably smaller than the primary hard phases, and have no significant influence on the wear resistance, such as for abrasive wear, but nevertheless they improve the supporting effect of the matrix. The cooling gradient has a decisive influence on the microstructure; with an increased cooling rate a finer-grain microstructure is formed than with a comparatively slow cooling.

Hard alloys are predominantly cast materials, the immediate use of which may be as cast parts, as cast welding filler materials, and/or as mechanically diminuted alloy powders, whether atomized or following the melting down of different components during application in thermal-coating processes. Besides full-material components, hard alloys are also available as coating materials [22, 23], in particular when the mechanical properties of the hard metals preclude their use as construction materials, for example as large-volume parts. The use of hard alloys as coating materials involves, on the one hand, cost advantages, since cost-effective materials such as low-alloy steels can be used as construction materials. Moreover, the substrate materials exhibit a greater toughness, such that the resistance to fracture of components manufactured in this way is improved. In the manufacture of such compound materials, various thermal coating processes – such as deposit welding, thermal spraying or deposit brazing – are employed. The coating thicknesses obtained with these processes range from a few hundred micrometers up to several millimeters. The welding, soldering, or spray filler metals may be used in the form of wire, powder, cored wire, or fleece [24]. In this case, self-flowing NiCrBSi alloys, FeCrBSi alloys and CoCrWC alloys (Stellite®; Deloro Stellite Holdings Corporation) are of particular technical importance.

5.2.5
Super-Alloys

The term "super-alloys" refers to all metallic materials intended for technical applications at high temperatures in excess of 540 °C; this includes Fe-, Ni-, and Co-based alloys. By far the most important area of application for super-alloys is gas turbine manufacture, particularly of the hot gas turbine components (such as rotor, blades and vanes) and the gas turbine combustor, where the prevailing conditions are high temperatures and large temperature discontinuities, as well as high pressures and large mechanical stressing. Generally, oxidizing and corrosive atmospheres are also superimposed over these peripheral conditions. Under such process conditions, the materials required must be capable of withstanding such stressing over long periods of time. The material limit for the high-temperature use of metallic materials is the onset of re-crystallization, as this causes a pronounced deterioration of the material strength. The contribution of the grain boundary strength drops off rapidly, together with the effect of most solidification mechanisms (see also Section 5.1.2).

Within the relevant temperature range for gas turbines ($T \sim 950$ °C substrate temperature), both Ni and Co super-alloys possess very high strengths [25] whilst, at the same time, exhibiting the most favorable ratio of density to strength (Figure 5.13). For these operating temperatures, common Fe-based alloys are no longer suitable, as they have a maximum re-crystallization temperature of approximately 800 °C, even when making use of all available alloying technology. Neither are refractory metals, nonoxidizing ceramics (Si_3N_4, SiC) and carbon fibers (C/C) suitable, for reasons of excessively high densities, insufficient stability against oxidation, insufficient fracture toughness, and poor machinability.

Figure 5.14 compares the creep–rupture strengths over 100, 1000, and 100 000 h for Fe-, Ni-, and Co-based alloys. As a basis for the calculation of unsteady gas turbines (e.g., in aircraft, where the engines are extensively overhauled within short time intervals), the 1000 h strength is decisive. However, for stationary plants (chemical plants and power plants), the 100 000 h strength is of primary interest. Whilst it is important to recognize the superiority of Ni and Co super-alloys compared to high-temperature steels, it is equally important to realize that, with increasing

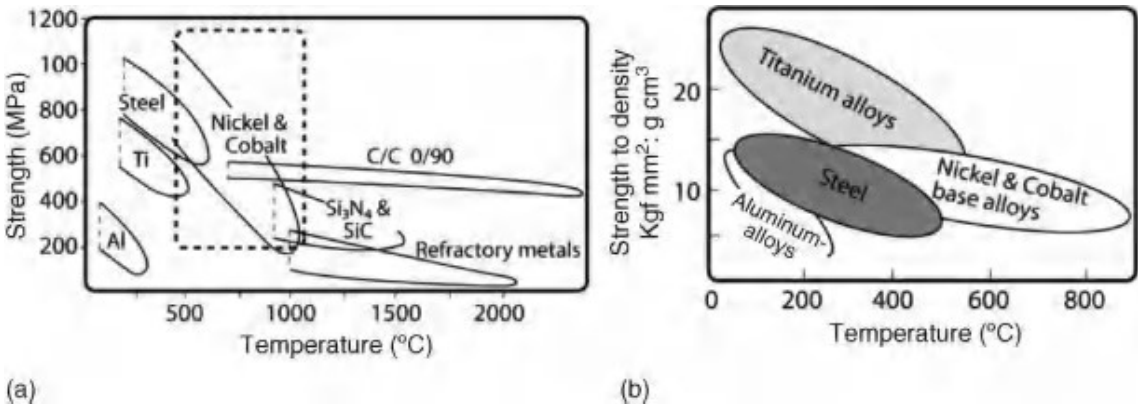


Figure 5.13 Temperature capabilities of material classes [26, 27].

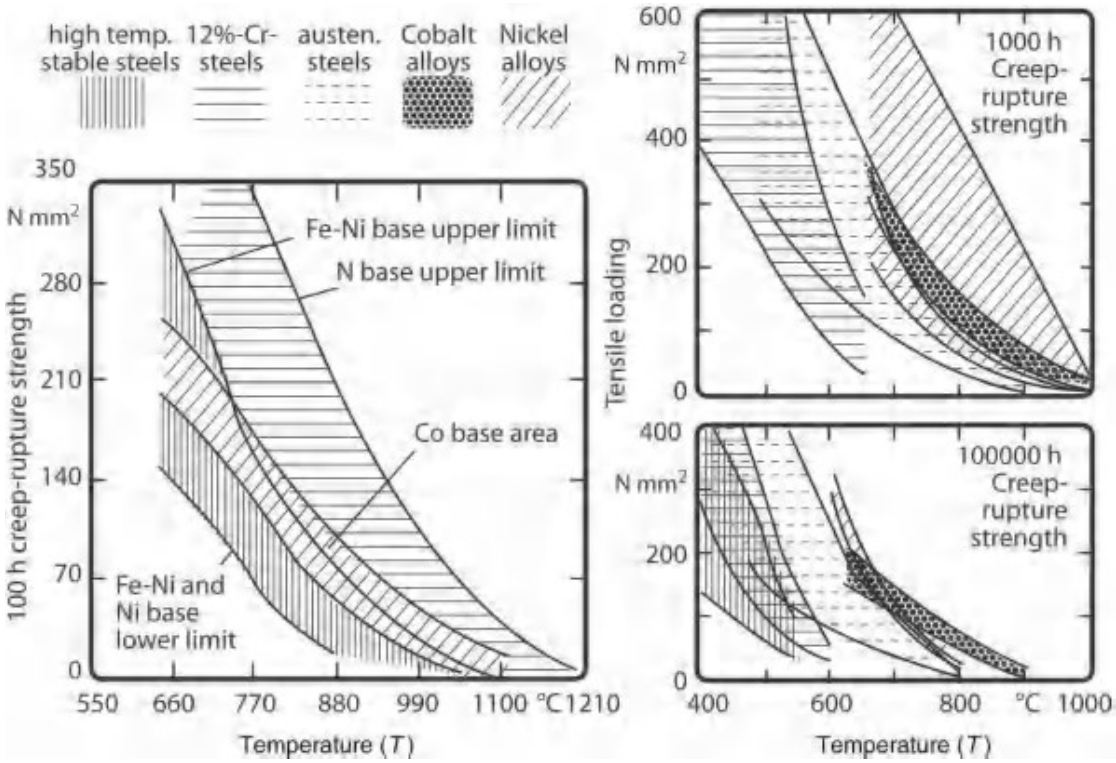


Figure 5.14 Creep–rupture strengths of the most important super-alloys.

stressing time and temperature, the superiority of Ni super-alloys is no longer so clear. It is for this reason that Co super-alloys are used preferentially in the field of power generation, while Ni super-alloys are used in aviation turbines (Table 5.15).

Super-alloys are classified according not only to their base metals, but also to their manufacture and further processing to cast and wrought alloys. Cast alloys allow the selective solidification of the microstructure and controlling of the grain size. In the ideal case, even single-crystal manufacture with excellent creep behavior is possible. The main purpose of wrought alloys, on the other hand, is the production of a very fine-grained microstructure with good forming properties and the possibility to produce a high dislocation density and formation under controlled conditions. This thermo-mechanical processing is employed almost exclusively for Ni-based materials. The production of the, mostly, semi-finished super-alloys takes place by way of melting in an electric furnace under a shroud gas, followed by continuous casting or diecasting and re-melting in vacuum in order to obtain the required degrees of purity and to minimize block-crystal segregation. In special cases – notably, when there is a desire to exploit the advantages of dispersion – powder-metallurgical production qualities have been introduced more recently, and these are also used for particularly fine carbide distributions. However, dispersion hardening is meaningful only for operating temperatures above 1000 °C, when the other hardening mechanisms fail. As strengthening elements, aluminum oxide and/or thorium oxide may be employed in so-called "oxide dispersion-strengthened" (ODS) alloys, either added directly to the powder mixture in aggregate form, or formed by internal oxidation in the material (Table 5.16).

Table 5.15 Commercially available nickel super-alloys and influence of the alloying elements.

Material no.	Commercial name	Composition (in wt%)									
		Co	Cr	Ni	Mo	W	Nb	Ti	Al	Fe	C
2.4668	Inconel 718	—	19.0	52.5	3.0	—	5.1	0.9	0.5	18.5	0.08
2.4665	Hastelloy X	1.5	22.0	49.0	9.0	0.6	—	—	2.0	15.8	0.15
2.4654	Waspeloy	13.5	19.5	57.0	4.3	—	—	3.0	1.4	2.0	0.07
Not known	M-252	10.0	19.0	56.6	10.0	—	—	2.6	1.0	0.75	0.15
Not known	Udimet 700	18.5	15.0	53.0	5.0	—	—	3.5	4.4	0.3	0.06
Not known	M-247	10.0	8.25	59.0	0.7	10.0	—	1.0	5.5	0.5	0.15
Cr	6–25 wt%	Improves resistance to oxidation and corrosion									
Fe	up to 20 wt%	Improves welding capability									
Co, Mo, W, Nb		Improves mixed crystal hardening									
Al, Ti, Nb		Forms coherent precipitations from the super-saturated mixed crystal, γ'-phases such as Ni_3Al, Ni_3Ti, Ni_3Nb, stable up to 800 °C									
Nb, Ti, Cr		Preferred carbide progenitor									

Table 5.16 Commercially available cobalt super-alloys and influence of the alloying elements.

Material no.	Commercial name	Composition (in wt%)									
		Co	Cr	Ni	Mo	W	Nb	Ti	Al	Fe	C
2.4989	S-816	42.0	20.0	20.0	4.0	4.0	4.0	—	—	4.0	0.38
2.4682	X-40	57.5	22.0	10.0	—	7.5	—	—	—	1.5	0.5
2.4964	Haynes 25	50.0	20.0	10.0	—	15.0	—	—	—	3.0	0.10
2.4683	Haynes 188	37.0	22.0	22.0	—	14.5	—	—	—	3.0	0.10
Cr	Improves resistance to oxidation and corrosion										
Cr, Nb, Ta, Ti	Preferred carbide progenitor, most important solidification mechanism										
Nb, Mo	Improves mixed crystal hardening										
W	Forms intermetallic precipitations, preferentially Co_2W and Co_3W										

5.2.6
Refractory Metals

Within the Periodic Table, transition metals belong to the d-block – that is, subgroups 3 to 12. Transition metals are distinguished by the fact that electron levels of higher order are filled before the shells of lower order are completely occupied. The same configuration of their outer electrons explains the similarities among the transition metals. Those transition metals with high melting points occupy subgroups 4 to 8, and the refractory metals subgroups 4 to 6. The term "refractory metal" derives from the Latin *refractarius* (= contrary, stubborn). Thus, the refractory metals are seen to have in common such properties as a high melting point (Figure 5.15), high densities, mostly high hardness and strength values, and a high modulus of elasticity (Table 5.17).

The transition metal with the lowest melting point is titanium ($T_S = 1660\,°C$). Refractory metals are non-noble and exhibit a high affinity for B, C, N, and O. When

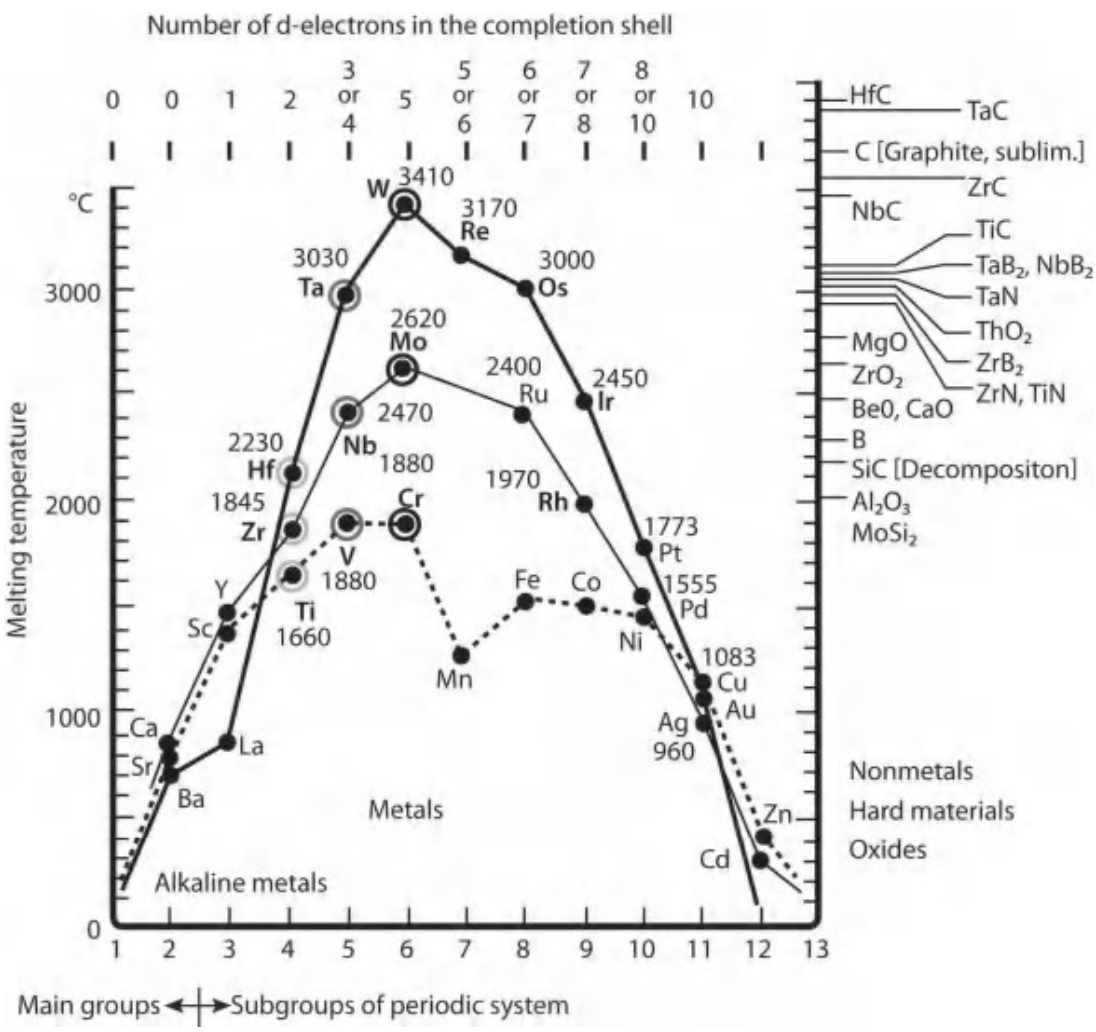


Figure 5.15 Melting points of metals, ordered in accordance with the Periodic Table.

Table 5.17 Properties of refractory metals.

	Symbol	Crystal structure	Density ϱ (g cm^{-3})	Melting point T_S (°C)	Modulus of elasticity (MPa)
Titanium	Ti	hcp > 882 °C bcc	4.51	1660	110 000
Zirconium	Zr	hcp > 862 °C bcc	6.51	1852	90 000
Hafnium	Hf	hcp >1760 °C bcc	13.31	2150	137 000
Vanadium	V	bcc	6.09	1890	137 000
Niobium	Nb	bcc	8.58	2468	103 000
Tantalum	Ta	bcc	16.68	2996	186 000
Chromium	Cr	bcc	7.14	1857	186 400
Molybdenum	Mo	bcc	10.28	2617	300 000
Tungsten	W	bcc	19.26	3407	405 000

exposed to the atmosphere, they form stable protective oxide layers (passive layers) on their surfaces, which is why they possess excellent corrosion resistance in many media. Because of their high tendency to react, their production is difficult, and must be conducted in complex shroud gas processes that require considerable energy input. Refractory metals are used primarily in the chemical industry, and also in reactor technology, furnace construction, and electro-technology. As alloying elements, they are indispensable in connection with Fe-, Ni-, and Co-based alloys. The carbides, oxides, nitrides and borides of the refractory metals are important hard materials for the design of tribological components.

5.2.7 Intermetallics

Intermetallics, which are better described as intermetallic phases, are formed from two or more metals with ordered lattices. Depending on the temperature, they show a more or less broad range of existence as a compound in the phase diagram. Intermetallics may be classified in two forms:

- The *daltonides* have a very narrow homogeneity range; that is, the range over which the composition of the alloy varies only very slightly from the stoichiometric composition (vertical line in the phase diagram).
- The *bertollides* show a more or less large deviation from the exact stoichiometry (concentration ranges in the phase diagram).

Although, strictly speaking, the term intermetallics is only correct when all of the elements involved are metals, it remains partly in use today and includes compounds such MoS_2 [28]. It has been documented that, as long ago as 2500 BC, in ancient Egypt, Asia Minor and Brittania, the intermetallics Cu_3As was used in the cementation process for the coating of bronze tools and other articles of practical value [29]. Westbrook has provided some extensive accounts of the history of intermetallics [29–32]. On the basis of the many possibilities for bonding, and the different sizes of

the participating atoms, a number of intermetallic phases exist, with some 5000 being recognized for binary phases alone [33].

When the forces of attraction between the different types of atoms are greater than between atoms of the same type, then compounds will be formed between the atoms of different types. According to their electrochemical behavior, compounds can form which show, in addition to purely metallic binding, partially covalent and ionic bonding. Thus, the description "intermediate phase" is an appropriate term, as the crystal lattice formed in intermetallics no longer leads to the properties of the participating single metals. This means that the properties of intermetallics can also not be derived from these. The resultant lattices are mostly very complex in terms of their structure, with an elementary cell perhaps including up to several hundred atoms. The crystal structures are mostly hexagonal close-packed, face-centered cubic or body-centered cubic. In spite of the great variety of intermetallic phases, it is possible to define a large number of rules that apply to certain groups of structures, and thus to predict the crystal structures within these groups [33]. The stability of intermetallics is determined essentially by the ratios of the atomic radii, the valence electron configurations, and the electronegativities of the components. According to whichever property is responsible for stability, it is possible to distinguish between Laves, Zintl, and Hume–Rothery phases. Although, in addition to these phases, other groups such as Hägg, Heusler or Frank–Kasper also exist, these will not be described at this point.

Laves phases: Among the classic intermetallic phases, the Laves phases constitute the numerically largest group [28], with several hundred representatives known to exist [33]. In the case of Laves phases, two inter-penetrating lattices, in which the atoms are not mutually in contact, are present in the form AB_2. These crystallize in the most densely packed lattice types, the hexagonal close-packed or face-centered cubic (Table 5.18). The most important characteristic of the Laves phases is the ratio of the radii r_A and r_B, which has a value of $1.2 < r_A/r_B < 1.3$ (1.225 [34]; 1.228 [35]). Due to the difference in the radii (>15%), Hume-Rothery phases or substitution mixed crystals can form. One decisive factor leading to predominantly metallic bonding is the difference in electronegativities, which is too small for the formation of ions. Moreover, the sum of the electronegativities is also small, so that the formation of covalent bonds is also not possible. Thus, which of the three lattice structures is ultimately formed is determined by the concentration of valence electrons.

Table 5.18 Stacking sequence for Laves phases [35].

Type	Lattice	Stacking sequence	Examples	Number
$MgCu_2$	fcc	ABCABC...	KNa_2, $BaPt_2$, $NaAg_2$, $CaAl_2$, KBi_2, YFe_2, TaV_2, $TiCo_2$...	500
$MgZn_2$	hcp	ABAB...	$CaLi_2$, $CsNa_2$, $BaPt_2$, $NaAg_2$, $TiMn_2$, $NbFe_2$...	350
$MgNi_2$	hcp	ABACABAC...	$TaCo_2$	50

Zintl phases: These are essentially formed between metals of groups 1 and 2 and elements of groups 14, 15 and 16, with the exception of C, N, and O. Sn and Pb also form such compounds and, in individual cases, so do Al, Ga, In, and Tl. On the basis of their physical properties, the Zintl phases are semi-conductors, and the tendency to form compounds is greater the more electropositive is one component and the more electronegative is the other. Both, binary and ternary Zintl phases have been identified. Compounds of the type AB have a common salt (NaCl) type lattice, while compounds of type AB_2 have a fluorospar (CaF_2) type lattice. Compounds of type ABC also have a fluorospar-type lattice. One common characteristic of Zintl phases is the ratio of the radii ($r_A/r_B \sim 1$–2.4).

Hume-Rothery phases: This common class of bonding is formed via the combination of transition metals with metals of the main groups, as well as Zn, Cd, and Hg which, as a result of their completely filled d-orbitals, behave in many ways as main group metals. In 1929, Hume-Rothery had already observed that, in the phase diagrams of certain binary chemical systems, the same sequence of phases was always present, and that the stability of the phases was related to certain concentrations of the electron cloud. The phases are determined by the valence electrons, such that the following general formulation of a compound A_mB_n applies:

$$\text{Valence electron concentration (VEK)}: \qquad \text{VEK} = \frac{mE_A + nE_B}{m+n}$$

where E_A and E_B are the valence electrons of the elements A and B.

The number of valence electrons of the transition metals of groups 8–10 is set to zero for the determination [36]. The metals Fe, Co, Ni and their homologues then clearly give up no electrons in these phases; the reason for this is most likely their tendency to completely (Ni, Pt) or almost (Fe, Co) maintain the d10 electron configuration (Table 5.19).

Table 5.19 Determination of the valence electron concentration and some examples of Hume-Rothery phases.

Phase	Lattice	Composition	Number of valence electrons	Number of atoms	Valence electron concentration
β-phase	bcc	CuZn, AgCd	1 + 2	2	3: 2 = 21: 14 = 1.50
		$CoZn_3$	0 + 6	4	6: 4 = 21: 14 = 1.50
		Ag_3Al	3 + 3	4	6: 4 = 21: 14 = 1.50
		FeAl	0 + 3	2	3: 2 = 21: 14 = 1.50
		Cu_5Sn	5 + 4	6	9: 6 = 21: 14 = 1.50
γ-phase	cubic[a)]	Cu_5Zn_8, Ag_5Cd_8	5 + 16	13	21: 13 = 1.62
		Fe_5Zn_{21}, Pt_5Zn_{21}	0 + 42	26	42: 26 = 21: 13 = 1.62
		Cu_9Al_4	9 + 12	13	21: 13 = 1.62
		$Cu_{31}Sn_8$	31 + 32	39	63: 39 = 21: 13 = 1.62
ε-phase	hcp	$CuZn_3$	1 + 6	4	7: 4 = 21: 12 = 1.75
		Ag_5Al_3	5 + 9	8	14: 8 = 21: 12 = 1.75
		Cu_3Sn	3 + 4	4	7: 4 = 21: 12 = 1.75

a) Cubic phase with its own structure.

As the intermetallic phases do not constitute a homogeneous group of materials, a general treatment of their properties is not possible. Nevertheless, all intermetallic phases can be said to have the common properties of high hardness and brittleness, essential to which is the formation of large elementary cells. In particular, the brittleness increases as the elementary cells become less symmetrical [37]. An additional common factor among intermetallic phases is that their properties are transferred to the entire alloy when they are produced via precipitation in technical alloys, and consequently their use must be carefully considered. Due to their many different phases, each with their own structures and special properties, the properties of the intermetallic phases can be described only for particular cases. From a technical standpoint, titanium-aluminides and nickel-aluminides represent the two most intensively investigated groups of intermetallic materials in recent years, with α_2-phase (Ti_3Al) and γ-phase (TiAl) having found their way into engineering applications. However, the most important phases of nickel aluminides have been recognized as γ'-phase Ni_3Al and β-phase NiAl.

5.3 Non-Metallic Inorganic Materials

The group of non-metallic inorganic materials includes not only ceramic materials but also glasses and semiconductors (though the latter will not be dealt with here). In respect of their chemical structure, these hard materials which, on the basis of their high hardness, chemical stability and good high-temperature behavior, are of major importance for tribological applications. Typically, hard materials find application as:

- precipitations in metallic alloys (see Section 5.2)
- hard particles or fibers in a metal, ceramic or polymer matrix with composite materials (see Section 5.5)
- coating materials (see Chapter 6)
- structural materials, such as engineering ceramics or high-performance ceramics (see Section 5.3.2).

5.3.1 Structure of Hard Materials

The term "hard materials" encompasses all materials with a Vickers hardness of more than 1000 HV [38]. Essentially, these are the carbides, nitrides, borides, silicides and oxides of the refractory metals (subgroups 4 to 6 of the Periodic Table). Other important elements which form hard materials are aluminum, silicon, and the rare earth metals, such as yttrium (Figure 5.16). Hard materials are solid interstitial solutions; that is, the non-metals C, N, and O or the metalloids B and Si occupy the interstitial positions of the metallic lattice structures, or

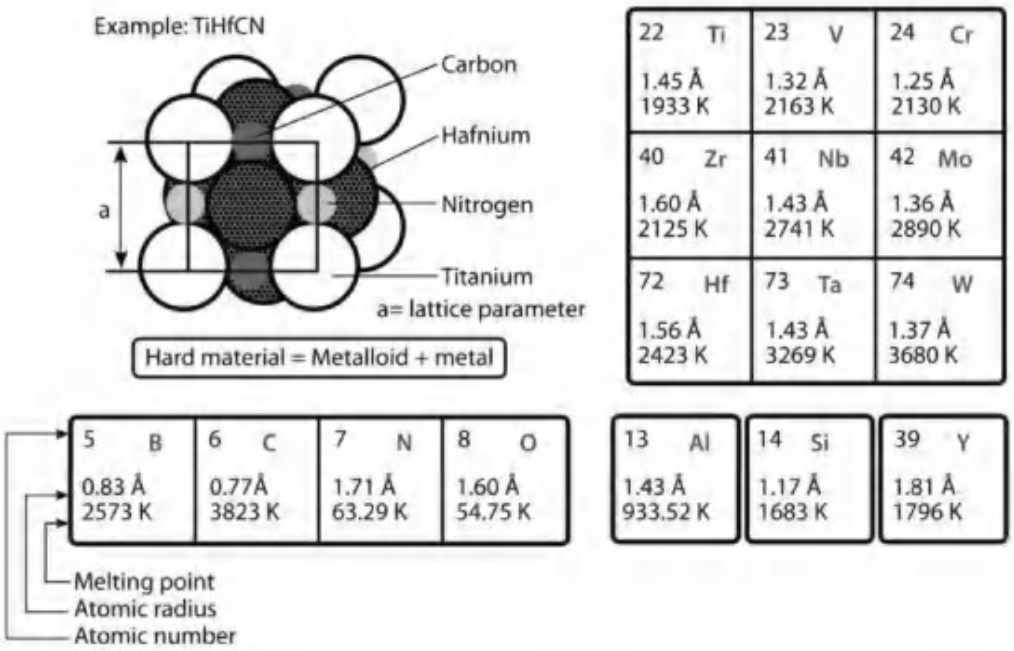


Figure 5.16 "Building blocks" for hard material systems [39, 40].

vice versa. Besides the high hardness values, the high melting points of hard materials especially stand out, these being above 2000 K for essentially all hard materials.

Classically, it is possible to differentiate between three groups of hard materials: (i) metallic hard materials; (ii) ionic (heteropolar) hard materials; and (iii) covalent hard materials (Figure 5.17). This classification is oriented to the character of the preferred chemical bonding. For technical hard materials, with the exception of diamond, different types of bonding exist in a hard material, though neither purely metallic nor purely ionic bonding will result in suitable hard materials [41]. Diamond is the only hard material which has *only* covalent bonding. The characteristic properties of the chemical bondings are decisive for the selection of the material.

Metallic hard materials are distinguished by good bonding to metallic alloys. In the composite system, this permits good cohesion between the metal matrix and the hard material particles, whilst on metallic substrates the best adhesion is achieved with metallic hard material layers. As a result of the high fraction of metallic bonding, metallic hard materials possess good thermal conductivity and comparatively good toughness compared to ionic and covalent hard materials (with the exception of diamond). Whilst the highest hardness values are obtained with covalent bonding, the greatest chemical stability on the surface is obtained with ionic bonding. This leads, on the one hand, to a favorable adhesive resistance, and on the other hand to very little tendency to react with the environment, even at higher temperatures. Ionic hard materials are good insulators. The material's behavior can be estimated according to its position in the "bonding triangle" (Table 5.20; Figure 5.17).

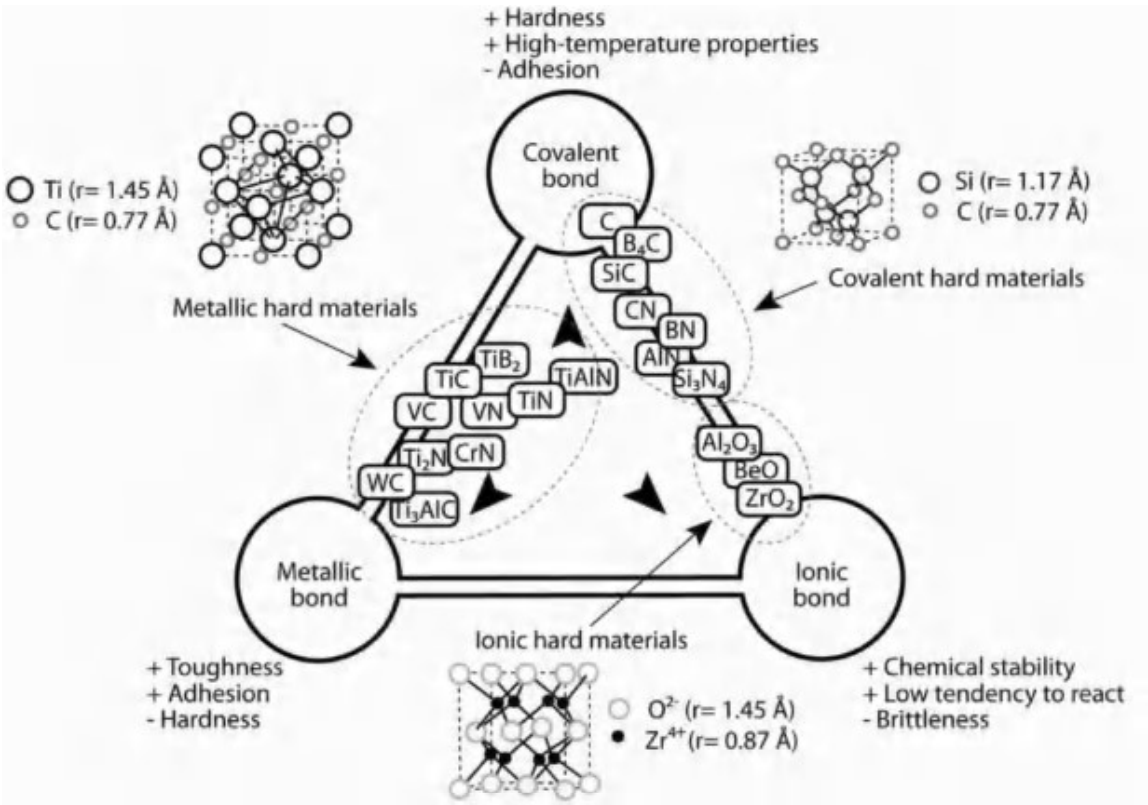


Figure 5.17 Classification of hard materials in the "bonding triangle" [42].

Table 5.20 Material properties depending on the character of their chemical bonding (after [43]).

Hardness	Brittleness	Melting point	Stability $-\Delta G$	Coefficient of thermal expansion	Adhesion to metals	Reaction tendency	
Covalent	Ionic	Metallic	Ionic	Ionic	Metallic	Metallic	↑
Metallic	Covalent	Covalent	Metallic	Metallic	Ionic	Covalent	→
Ionic	Metallic	Ionic	Covalent	Covalent	Covalent	Ionic	↓
Borides	Oxides	Carbides	Oxides	Oxides		Borides	↑
Carbides	Nitrides	Borides	Nitrides	Nitrides		Carbides	→
Nitrides	Carbides	Nitrides	Carbides	Carbides		Nitrides	→
Oxides	Borides	Oxides	Borides	Borides		Oxides	↓

5.3.2
Engineering Ceramics

In applications where hardness and wear resistance, chemical and thermal stability, and a good weight-to-strength ratio are required, metallic materials are unable to sufficiently satisfy these demands, or indeed to satisfy them at all. In this case,

ceramic structural materials – which are also known as engineering ceramics, technical ceramics or high-performance ceramics – offer very promising alternatives. However, along with these positive features there are also negative properties, such as excessive brittleness, (in part) a poor thermo-shock stability, difficulties with machining, and a broad scattering of characteristic values. In respect of their classification, engineering ceramics can be divided into three main groups: oxide ceramics; non-oxide ceramics; and silicate ceramics. One important distinguishing feature is the glass phase fraction, which can be considerable for silicate ceramics but very low or even non-existent for oxide and non-oxide ceramics. As a rule, engineering ceramics are formed at room temperature from a raw mixture, and take on their typical material properties, usually as the result of a high-temperature sintering process.

5.3.2.1 **Oxide Ceramics**

Among oxide ceramics, aluminum oxide (Al_2O_3), zirconium oxide (ZrO_2) and aluminum titanate ($Al_2O_3 \cdot TiO_2$ or Al_2TiO_5) are the most important technical materials, while the use of beryllium (BeO), magnesium (MgO), thorium (ThO_2), and titanium (TiO_2) oxides and spinel ($MgO \cdot Al_2O_3$ or $MgAl_2O_4$), at least as structural materials, is limited to special cases. The properties of oxide ceramics are determined by the prevailing fractions of ionic and covalent bonding. The stability of these bonding types is responsible for the properties already mentioned, such as thermal stability and corrosion resistance, in addition to the insulating properties important for electrical and electronics applications.

Al_2O_3 constitutes the greatest share of the market and finds application as cutting ceramics, blasting shot and wear-protection coatings [e.g., chemical vapor deposition (CVD), physical vapor deposition (PVD), or thermal spraying]. In order to improve the thermo-shock stability and fracture toughness, Al_2O_3 is manufactured as a mixed ceramic, together with TiO_2, TiC or ZrO_2 (zirconium-toughened alumina; ZTA). Far better behavior in respect of cyclical thermal and mechanical loading is shown by ZrO_2, which is used for example, as a protective coating in combustion engines. In order to suppress the allotropic phase transformation (monoclinic $\rightarrow$ tetragonal) of pure ZrO_2, it is used almost exclusively with stabilizers, the most frequently used stabilizer being Y_2O_3, added in amounts of 3–8 wt%. The addition of 8 wt% Y_2O_3 fully stabilizes the cubic phase (fully stabilized zirconium oxide; FSZ). As a rule, partially stabilized zirconium oxide (PSZ) is employed, in which the tetragonal phases are present in a cubic matrix [44].

5.3.2.2 **Non-Oxide Ceramics**

The term "non-oxide ceramics" describes all ceramic materials manufactured on the basis of borides, carbides, and nitrides. Besides diamond (C), the most important representatives are silicon nitride (Si_3N_4), silicon carbide (SiC), aluminum nitride (AlN), boron nitride (BN), and boron carbide (B_4C). By contrast with oxide ceramics, predominantly covalent bonding is found in non-oxide ceramics. As the participating elements, such as B, Al, Si, C, and N have small atomic diameters, the atomic spacing is small and the binding energy accordingly high.

This is (in part) the reason for the exceptionally high mechanical and thermal stability, which is reflected in the high hardness values and high melting points. For example, cubic boron nitride (cBN), with a Knoop hardness of 4650 HK100, has the highest hardness value of all known substances, except for diamond. The immense influence of the lattice type on the properties becomes apparent with the extremely low Knoop hardness of 6–30 HK100 for hexagonal boron nitride (hBN), which is also referred to as "white graphite." Whereas, cBN may find application as a cutting material, hBN is known to be an excellent solid lubricant for high-temperature applications.

5.3.2.3 **Silicate Ceramics**

Silicates are the salts and esters of *ortho*-silicic acid ($Si(OH)_4$) and its condensates. The Earth's crust is comprised almost entirely (>90%) of silicates and, indeed, silicate ceramics constitute the oldest group of all ceramics. The most important component is clay or kaolin, derived from feldspar and soapstone. In addition, alumina (γ-Al_2O_3) and zirconium are used to obtain certain special material properties, such as high strength. During the sintering process, a high glass phase fraction (predominantly of SiO_2) is usually formed in addition to the crystalline phases [45]. Silicate ceramics include:

- porcelain (alkaline aluminum silicates)
- steatite (magnesium silicates)
- cordierite (magnesium–aluminum silicates)
- mullite ceramics (mullite: $3Al_2O_3 \cdot 2SiO_2$ and corundum: Al_2O_3).

5.4 Organic Materials

The diverse use of polymers is the result of their relatively simple processing, comparatively inexpensive raw materials, favorable mechanical properties, and relatively low densities, in the range of 0.9 to 2.2 $g\,cm^{-3}$. The processability and mechanical properties can be influenced over a wide range by a suitable choice of additive materials, such as softening agents, stabilizers, lubricants and filler materials [8]. Of advantage are the low processing temperatures of approximately 250–300 °C for injection molding and extrusion production processes.

All polymers have in common the fact that they are essentially comprised of organic materials with macromolecular structures. The smallest structural elements are low-molecular-weight reactive molecules (monomers), that are linked by polymerization, polyaddition or polycondensation to form macromolecules (polymers) [46]. The macromolecular polymers produced in this way, in contrast to the cubic or hexagonal microstructure of metal atomic lattices, exhibit a filamentous or netted structure [47]. The most important monomers for the production of polymers are unsaturated low-molecular-weight carbon compounds (i.e., with C=C double bonds [46]), which are derived primarily from crude oil, but may also be produced

from natural gas or carbon:

- ethene (ethylene) C_2H_4
- propene (propylene) C_3H_6
- butene (butylene) C_4H_8
- ethine (acetylene) C_2H_2
- butadiene C_4H_6
- benzene, toluene C_6H_6.

The linking of carbohydrate molecules to molecular chains (polymers) can take place by way of bonding between carbon atoms or by way of sulfur, nitrogen, or oxygen atoms. With C–C, C–N, C–O and C–S bonding, covalent bonding ensures a stable cohesion along the molecular chain, and this constitutes the main valence bonding. In addition to carbon, silicon can also form macromolecules by way of oxygen bridges, for example, polysiloxane: –Si–O–Si–. Bonding between different monomers results in "copolymers" – that is, regular arrangements of molecular blocks, or so-called "block polymers." The cohesion of the molecular chains amongst each other derives from van der Waals forces (so-called "semi-valence bonding"), which is several orders of magnitude weaker than covalent binding energies. The forces of attraction can be attributed to the overlapping of molecular orbitals, or to the electrostatic interaction between permanent or temporary dipole molecules, whereby the formation of hydrogen bridges between neighboring oxygen and hydrogen atoms contributes the strongest binding energies. When subjected to tensile loading, polymers fail due to the severing of the semi-valence bonding (Figure 5.18), and this results in low strength values of around 10–100 MPa [46]. In contrast to metals, many polymers are – because of their organic character – stable in the presence of inorganic media, including mineral acids, lyes, and aqueous salt solutions. However, also in contrast to metals, they react sensitively with organic solvents, such as alcohols, acetone, and benzene. Nevertheless, it has been possible to develop polymers which are stable in the presence of these media; one such example is the polyethylene petrol tank in the Volkswagen Polo which, simultaneously, is highly resistant to atmospheric corrosion and insensitive to petrol.

Polymers with linear or branched molecular chains in their ultimate form are known as *thermoplasts* (Table 5.21). These can be re-melted; in other words, the

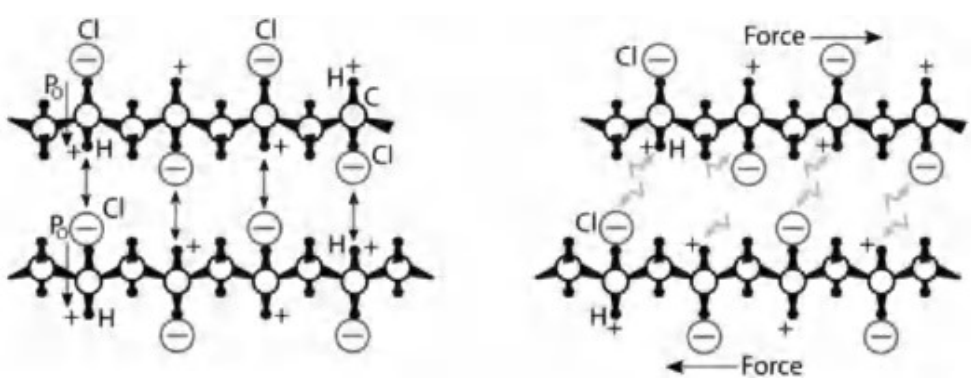
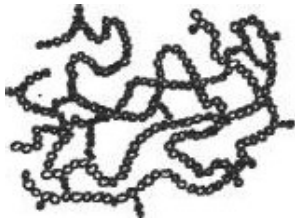
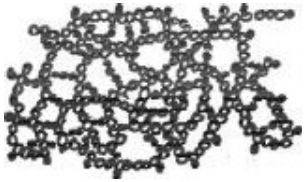


Figure 5.18 Breaking of semi-valence bonds as a result of tensile loading for the example of polyvinyl chloride (PVC) with van der Waals dipole bonding between Cl^- and H^+.

Table 5.21 Classification of plastics according to their molecular structure.

Thermoplasts		Elastomers	Duroplasts
			
Linear molecular chains	Branched molecular chains	Weakly networked molecular chains	Strongly networked molecular chains
Capable of melting		Not capable of melting	Not capable of melting
Soluble		Capable of swelling	Not capable of swelling
For RT soft to hard-tough or hard-brittle		Not soluble	Not soluble
		For RT elastically soft	For RT hard

application of heat can alter the relative spacing of the molecular chains, so that they can slip over each other, causing them to be flowable and providing them with good shaping properties. However, when the molecular chains are linked to each other ("networked"), they can no longer be re-melted. A wide-meshed networking enables the formation of *elastomers*, and a close-meshed linking to so-called *duroplasts* (also referred to as *duromers*) (see Table 5.21) [48].

5.4.1 Thermoplasts

Thermoplasts are easily plastically deformable over a certain temperature range (they are then termed *thermoplastic*). Thermoplastic products can be manufactured by using primary shaping and forming processes, followed by machining. Below the decomposition temperature, thermoplasts can be repeatedly re-melted, which makes them suitable for recycling and also for welding. In thermoplasts, which represent the largest group of polymers currently in use (Table 5.22), there is no covalently bonded networking between the molecular chains. Completely disordered molecular chains forming an intertwined cluster are referred to as *amorphous* thermoplasts, while *semi-crystalline* thermoplasts are characterized by molecular chains in a parallel arrangement, according to the degree of crystallization (Figure 5.19).

Table 5.22 Typical thermoplasts and examples of their applications.

Abbreviation	Material name	Examples of applications
PA	Polyamide	Gearwheels, plain bearings, plain rollers, textiles, carpets
PC	Polycarbonate	CDs, DVDs, automotive glass, optical lenses, eyeglass lenses
PEEK	Polyether ketone	Rolling bearing cages, medical technology (stable up to 335 °C)
PET = PETP	Polyethylene terephthalate	Recyclable bottles, textile fibers, vascular prostheses
ABS	Acrylonitrile butadiene styrene	Automotive parts, Lego bricks, do-it-yourself equipment
POM	Polyoxymethylene, polyformaldehyde	Plain bearings, gearwheels, pump components, fan impellers, valve bodies
PMMA	Polymethyl methacrylate	Dental prostheses, tail lamps, reflectors, watch glasses, eyeglass lenses
PE-UKMW	Ultra-high molecular polyethylene	Pump components, gearwheels, sliding bushings, implants, endoprostheses
PP	Polypropylene	Crash absorbers, child seats, bicycle safety helmets, seals
PTFE	Polytetrafluoroethylene	Plain bearings, shaft seals, vascular prostheses, non-stick coatings

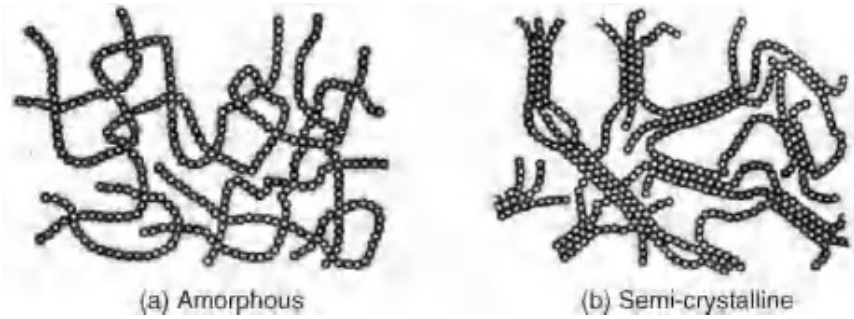


Figure 5.19 Molecular structures of thermoplasts. (a) Amorphous; (b) Semi-crystalline.

Table 5.23 Typical duroplasts and examples of their applications.

Abbreviation	Material name	Examples of applications
UP	Unsaturated polyester resin	Fiber-reinforced material components, buttons, heat-resistant and electrically insulating handles for cooking pots and pressing irons
EP	Epoxy resin	Fiber-reinforced material components for aviation and aerospace and automotive construction, structural adhesives (e.g., in boat constructions)

5.4.2 Duroplasts

Duroplasts are hard, glass-like polymer materials that are three-dimensionally networked via main-valence bonding. As the linkage is thermally stable, the duroplasts have neither melting capability nor swelling capability; moreover, they are stable in relation to solvents, and cannot be recycled. Their manufacture frequently takes place by way of polycondensation when, after hardening, they are no longer capable of plastic deformation. Duroplasts are used in the manufacture of light switches, and also frequently as components of fiber-reinforced materials (Table 5.23) [46].

5.4.3 Elastomers

Elastomers, which are also known as *rubber* or *vulcanized rubber*, are produced by the main-valence-bonded (chemical) networking of caoutchouc [49]. In 1839, the inventor, Charles Goodyear, found that when caoutchouc was subjected to heat with the addition of sulfur, it was transformed into rubber, in a process known as *vulcanization*. Like duroplasts, elastomers are thermally stable and cannot be re-melted, although compared to duroplasts they are only weakly networked. Up to the decomposition temperature, but also at very low temperatures, elastomers exhibit a pronounced

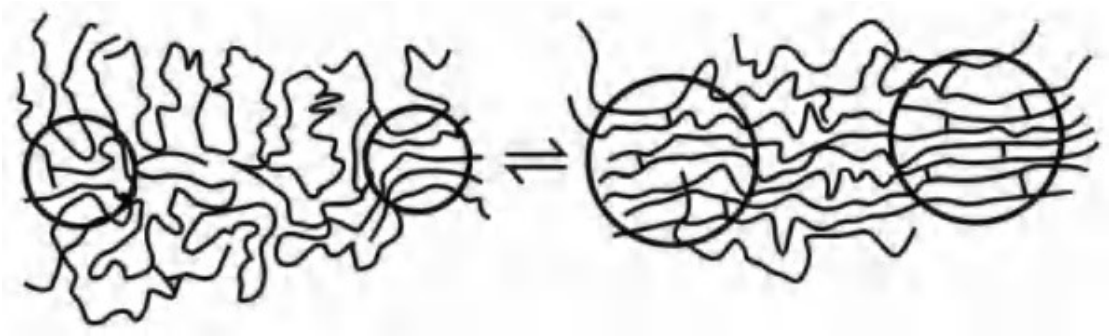


Figure 5.20 Elastic behavior of elastomers due to the stretching and contraction of the molecular chains.

Table 5.24 Typical elastomers and examples of their applications.

Abbreviation	Material name	Examples of applications
NR	Natural rubber	Rebound rubber, sand-blasting hoses, rubber-metal bearings, engine mounts, tires, bridge bearings, structural bearings
SBR	Styrene-butadiene rubber	Tires, rubber articles, conveyor belts, shoe soles
EPDM	Ethylene-propylene-diene rubber	Foamed automotive door seals, O-rings, floating ring seals, flat packings
NBR	Nitrile rubber	Seals, membranes, medical gloves, conveyor belts

elastic deformability. Such elasticity is due largely to the ability of the intertwined polymer chains to react to tensile loading by stretching, together with a disentanglement of the chains (Figure 5.20). Following removal of the tensile load, the chains again relax to their intertwined state. In order to prevent slipping of the chains over each other under tensile loading, the molecules are interlinked by sulfur bridging. The addition of a large amount of sulfur leads to the production of hard rubbers via vulcanization, whereas the addition of small amounts of sulfur leads to soft rubbers (Table 5.24).

5.5 Composite Materials

Within the field of composite materials, the continuously expanding requirements placed on technical components have prompted intensive research activities, as the combination of different materials has allowed the production of new materials with greatly improved properties. Composite materials are multiphase, macroscopic, homogeneous systems with phases of different principal material groups. The classification of composite materials is made according to the matrix material

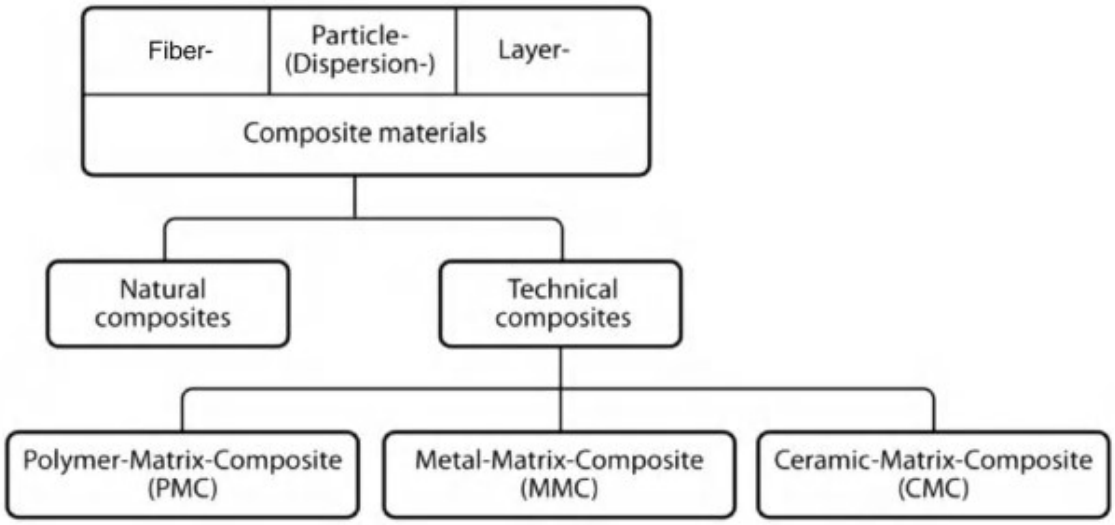


Figure 5.21 Classification of composite materials according to the matrix system.

(polymer, metal, ceramic) and the structure of the strengthening component (Figure 5.21). In this section, only composite systems of technical interest will be discussed.

In the case of a composite material, the matrix is reinforced with fibers, particles or layers in order to selectively improve certain properties. Such specific properties are the ratio of the tensile strength to the density (R_m/ϱ), and the ratio of the modulus of elasticity to the density (E/ϱ). These are determined by the properties of the matrix, and the strengthening components and their geometry and spatial arrangement (Figure 5.22). The interfacial boundaries between the matrix and the strengthening components may also have a considerable influence in this respect.

The strengthening components serve to bear the greatest part of the load acting on the component. The matrix, on the other hand, supports the strengthening components, provides cohesion and transfers the loads acting, as well as assimilating compressive loading and protecting fibrous composite materials for example, against buckling. The matrix also protects the strengthening components against ambient chemical attack. Depending upon the matrix material, polymers and metallic or ceramic materials are suitable as strengthening components.

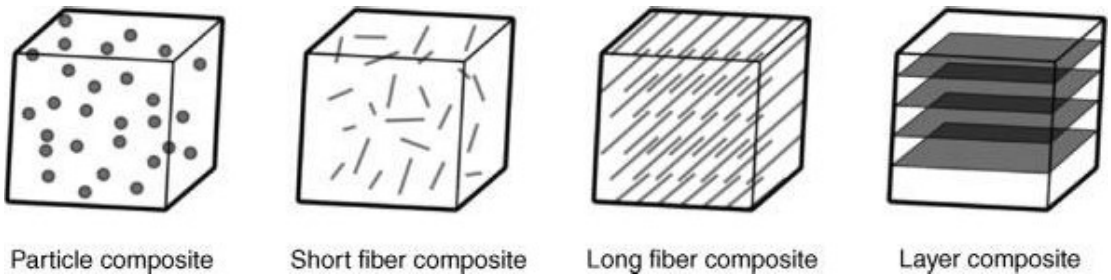


Figure 5.22 Basic composite material systems.

Fibers (long fibers, short fibers, long-fiber fabric): A distinction is made between short and long fibers. Long fibers can also be utilized as semi-finished textiles, in the form of fabrics or meshwork. Of technical importance are:

- carbon fibers (graphitic structure)
- glass fibers (SiO_2 with Ca, B, Al)
- aramide fibers (aromatic polyamides)
- polyethylene fibers (PE)
- boron fibers (C fibers with boron coating applied by CVD or W wires)
- ceramic fibers (SiC, Al_2O_3 partly stabilized with B_2O_3 and/or SiO_2)
- metallic fibers (W wires)
- metal carbide fibers (selectively solidified eutectic alloys, for example, Co–Cr–C or Co–Cr–TaC).

Modern fibrous composite materials find application as lightweight, high-strength components in the areas of aviation and aerospace engineering, as well as in the automotive industry, particularly in racing vehicles and in the high-price market segment. Increasingly, these materials are also finding use in the sports industry.

Particles and dispersions: Composite particle materials with hard material particles (oxides, borides, carbides, nitrides, silicides) are primarily employed as abrasive wear protection. They are the most commonly employed strengthening process, and are utilized with polymers, as well as with metals and ceramics. The strengthening effect of finely distributed hard particles in a metallic matrix derives from the impeding of dislocation movements. Here, there are two possible mechanisms. According to the Kelly–Fine theory, the particles are penetrated by the dislocations, whereas the theory of Orowan postulates that the dislocation lines migrate around the particles, leaving behind a dislocation ring around the particle. Both mechanisms absorb energy and therefore slow the migration of dislocations, thus enhancing the strength. By contrast with precipitations, embedded impurity particles (dispersions) are not soluble in the matrix at high temperatures, and therefore offer improved heat resistance. In electrochemically deposited dispersion coatings (see also Section 6.2.5), graphite, MoS_2 and polytetrafluoroethylene (PTFE) particles are also embedded to reduce friction. A frequently used filler material in natural rubber mixtures is carbon black which, besides its strengthening effect, also enhances ultraviolet (UV) stability and can be used to produce electrically conductive polymers [46].

Whiskers: Capillary single crystals with diameters $D \leq 1\,\mu m$ are known as whiskers. Because of the lack of grain boundaries and virtual absence of lattice defects, their strengths are of the same order of magnitude as the theoretical values for ideal crystals. In metals, considerable improvements in performance have been demonstrated using SiC and Al_2O_3 whiskers, while the use of boron whiskers and whiskers of different metals have also shown improvements. In spite of their excellent mechanical properties, however, the use of whiskers has not become established, the main reason being the health hazards that can arise from the ingestion/inhalation of particle sizes similar to those of asbestos.

5.5.1
Polymer Matrix Composites (PMC)

The addition of filler particles can improve the mechanical properties and abrasion resistance of polymers. Best suited for this purpose are kaolin (aluminum silicate), lime (calcium carbonate, $CaCO_3$), glass beads, stone dust, siliceous sand, and to some degree, also carbon black [46]. Fiber-polymer composites (FPCs) contain carbon fibers, glass fibers, aramide, or polyethylene (PE). Although currently duroplasts are primarily employed as the matrix material for FPCs, the use of thermoplasts has shown a fairly rapid increase [46]. The manufacture of components from composite polymer materials can be divided into three process steps:

- The strengthening components are introduced; these may be in the form of long fibers, fabrics or meshwork, as well as pre-impregnated semi-finished materials ("prepregs").
- The fibers are infiltrated into the polymer matrix.
- The composite materials are hardened (duromer matrices) or cooled (thermoplasts).

5.5.2
Ceramic Matrix Composites (CMCs)

Ceramic structural materials are distinguished by a number of properties, which makes them superior to polymers or metallic materials for certain applications. In particular, they have a high tensile strength and rigidity, even at high temperatures, they are characterized by a low specific weight and, in general, they have a good chemical stability. One disadvantage of many technical ceramics, however, is their low fracture toughness and the related low damage tolerance for defects. This means that even tiny defects, especially on the surface, may serve as the starting point for cracking. Due to their poor plastic deformation and the resulting reduction of stress peaks, even slight defects can lead to component failure. In contrast to polymers and composite metal materials, the strengthening of the matrix is required primarily to improve the damage tolerance. Here, the introduction of fibers to the ceramic matrix can hinder or even stop the propagation of cracks by initiating energy-absorbing processes, such as the tearing out of fibers, and the branching or redirection of cracks [50]. The ratio of the modulus of elasticity of the strengthening components to that of the matrix is therefore low. In the extreme case, both phases have the same rigidity. The development and application of composite ceramics essentially makes use of C and SiC fibers and, to a limited extent, of Al_2O_3 fibers. Likewise, Al_2O_3, mullite ($3Al_2O_3 \cdot 2SiO_2$), C and SiC have also been employed as matrix materials for technical applications [51].

Although, developments aimed at improving the fracture toughness of engineering ceramics by the embedding of particles, single crystal fibers (whiskers) or flattened particles (flakes) have improved their cracking resistance only to a limited extent, they have led to applications in oxide ceramic cutting tools (Al_2O_3). Drastic

improvements in cracking resistance and improvements of properties such as ductility, fracture toughness and thermo-shock stability resistance, might also be realized by using C/SiC for the brake discs of automobiles.

5.5.3 Metal Matrix Composites (MMCs)

The particle and fiber reinforcement of metal alloys can take place in two different ways: (i) particles can precipitate out during solidification of the melt (precipitation hardening); or (ii) be added as dispersions (dispersion hardening). By the selective solidification of a eutectic alloy, fibers can be formed or incorporated by re-melting with the molten metal. As the mode of action of precipitations and selective solidification has been discussed previously (see Section 5.2), the following will be limited to the introduction of impurities as strengthening components (Table 5.25) for the MMCs. Due to the high melting points of the metallic alloys, it is necessary to take into consideration any chemical interactions between the impurity particles and fibers and the metallic melt. This presents no problems for the electrochemical deposition of dispersion coatings from aqueous electrolytes (see also Section 6.2.5), in which temperature-sensitive particles, such as PTFE, can also be embedded.

From the tribological standpoint, MMC systems can be divided into two groups with application-specific objectives:

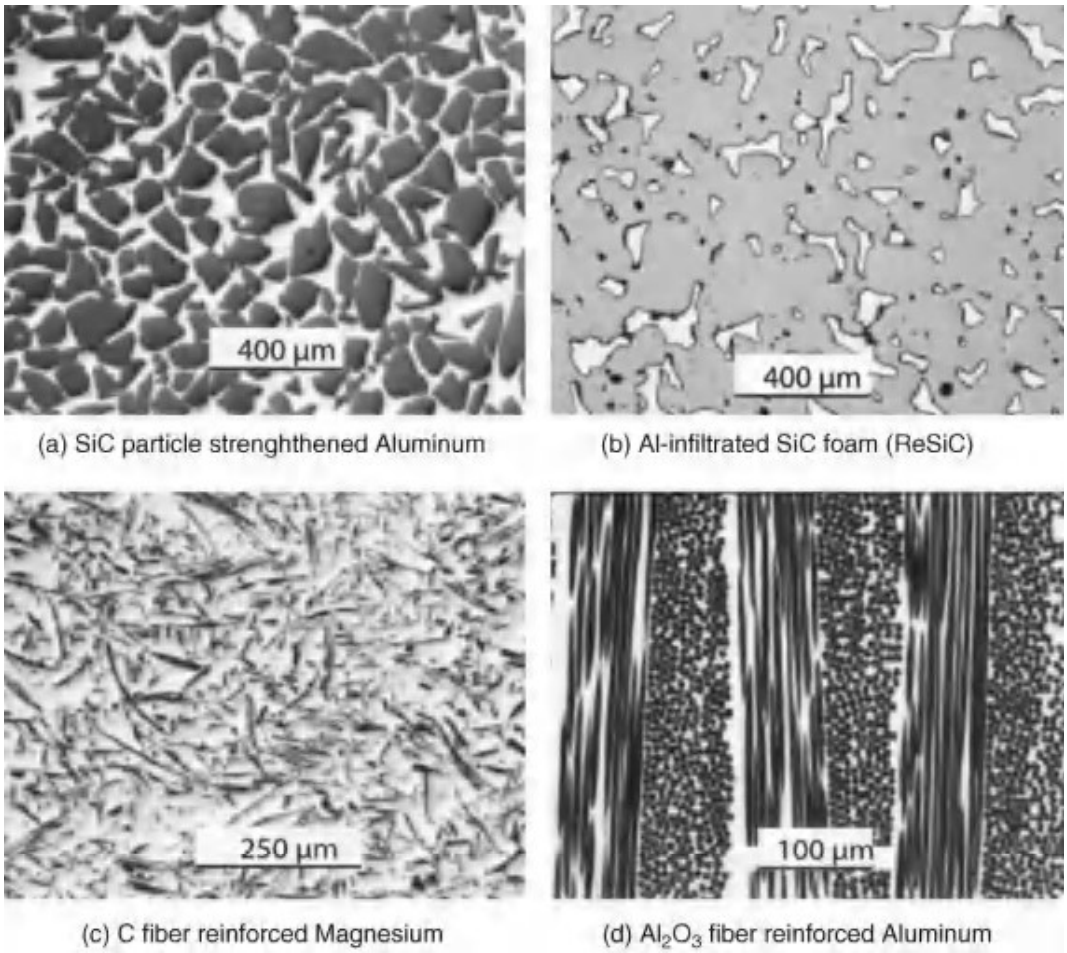
- The strengthening of lightweight metals (Al, Mg, Ti), to improve their tribological, thermal, and mechanical loading capacities.
- A maximum wear resistance with metal–hard material composites, having the best possible combination of high hardness and high toughness, with Co, Ni, and Fe-based alloys as the matrix metals.

5.5.3.1 MMCs for Lightweight Constructions

Today, the range of applications for lightweight metal components is continually growing, with lightweight structural components – notably composed of aluminum but also of magnesium or titanium – having become standard in many areas, particularly in the automotive and aviation/aerospace industries. Although such lightweight metals have their limits when they must withstand high tribological, mechanical, or thermal loadings, their application limits can be extended by

Table 5.25 Strengthening components used in MMCs.

Type	Aspect ratio	Diameter (μm)	Examples
Particles	1–4	0.1–150	SiC, Al_2O_3, cBN, B_4C, WC, WC/W_2C, TiC, TaC, TiCN, NbC, Mo_2C, VC, Cr_3C_2, diamond
Short fibers	10–10 000	1–5	C, SiC, Al_2O_3, $Al_2O_3 + SiO_2$
Long fibers	>1000	3–150	C, B, W, Nb–Ti, Nb_3Sn, SiC, Al_2O_3



(a) SiC particle strenghthened Aluminum
(b) Al-infiltrated SiC foam (ReSiC)
(c) C fiber reinforced Magnesium
(d) Al_2O_3 fiber reinforced Aluminum

Figure 5.23 Photo-micrographs of reinforced lightweight metal alloys.
Source: EMPA, Switzerland [52].

strengthening them with particles and with short and long fibers, usually of SiC, Al_2O_3, and C (Figure 5.23) and, in part, also with B_4C. Both, fiber- and/or particle-reinforced composite lightweight metals can be manufactured in different ways; the simplest of these is the preferential addition of particles or short fibers to the metallic melt, followed by casting in the absence of any pressure. In order to obtain the most homogeneous distribution of the strengthening components possible, the melt must be stirred. Since the components manufactured in this way have no preferred direction of strengthening components in their microstructures, the material properties will be isotropic. In particular, sub-eutectic aluminum–silicon alloys are processed in this way. The addition of strengthening components increases the viscosity of the melt, limiting the maximum fraction of the strengthening components to approximately 30 vol% [52]. Then, by using a die-casting processes, previously manufactured semi-finished materials (preforms) of strengthening components may be infiltrated with metallic matrices. Such semi-finished materials are produced, for example, from short fibers dispersed in water, when the mix is pressed into a form and then dried. For the manufacture of MMC components, the

pre-formed porous semi-finished material is first introduced into a heated form, after which the metallic melt is driven into the mold by applying a pressure of 70–100 MPa (the pressure can be applied mechanically by a ram, or by using a pressurized inert gas). By using this process, it is possible to manufacture components with a fiber content of up to 80 vol% [52]. In particular, low-melting alloys (Al, Mg) are preferentially processed via this method. It is also possible to introduce long fibers and/or also fabric or foam into a metallic matrix by using similar processes. Unfortunately, the casting process has one major disadvantage, in that the fiber distribution is poorly controlled to a point where pre-fabricated semi-finished goods may not be present. A better distribution of the strengthening components can be achieved by using a powder-metallurgical manufacture. In this case, the ceramic particles are mixed with the matrix metal (which is present in the form of a powder) in order to obtain a homogeneous distribution in the component. The mix produced in this way is then compacted in a subsequent process step to create a green body, the density of which is about 80% that of the final product. In order to dehumidify the green body, the semi-finished material is first de-gassed under low pressure, after which the green body is further compressed, but this time at high temperatures. The product produced in this way can serve as the starting material for further processes, such as extrusion, forging, or rolling, whereby the particle size is then limited to 40 vol% in order to ensure good shaping properties.

5.5.3.2 MMCs for Maximum Wear Resistance

Wear protection in MMCs is achieved by particle strengthening, using hard materials. This development began during the very early 1900s, with the invention of the electric-arc furnace and the investigations conducted by Moissan, who used this system to produce artificial diamond. Although, in fact, diamond was not produced, some very hard compounds of tungsten and carbon were created that would soon be recognized as important in engineering [53]. Further research and development was conducted by the lamp industry with the successful manufacture of filaments from tungsten; however, as this required the use of very costly diamond drawing tools, a more cost-effective alternative was sought. Unfortunately, the initial attempts at using hard carbides to manufacture molds for tools and parts that were most subjected to wear proved to be unsuccessful. Consequently, two alternative approaches were pursued, and this led to the material concepts used today for extreme wear stressing.

The first approach followed the enrichment of alloyed steels with metal carbides. In addition to the alloyed steels used initially, Tamman achieved positive results with Ni–Cr and Co–Cr alloys, such that hard alloys (see also Section 5.4) were first developed at the start of the twentieth century. When using this melt-metallurgical method, the carbide content was limited to 45 vol%, since above this value the alloys could no longer be forged and, for many applications, were too brittle. However, with the introduction of powder metallurgy, it became possible to increase the particle content to more than 50 vol%. The so-called "pseudo-alloys," which comprise a matrix of hard alloy and hard material particles (preferably of WC, VC, Cr_3C_2 or fused tungsten carbide WC/W_2C) are widely used in mining, strip mining, in the

construction industry, and for the extraction of materials. These are processed via thermal deposition welding coating processes (see also Section 6.2.7), thermal spraying (see also Section 6.2.6), and deposition brazing (see also Section 6.2.8), with powders, cored wires or fleeces being employed as filler materials. During the course of development, the range of hard materials was extended such that, today, borides, cBN, B_4C and diamond are all also used for strengthening. Nonetheless, the carbidic hard materials – which are distinguished by their excellent bonding to the metal matrix due to the high fraction of metallic bonding in the metal carbides – continue to dominate. Currently, sintered, tempered and annealed TiC–Fe composites with hardening capabilities are successfully employed as wear-resistant materials in ship building, sheet metal-forming, and compression molding under the designation "ferrotitanites." These alloys contain approximately 50 vol% TiC, while the matrix is comprised of steels of different compositions (tool steel, heat-resistant steel, etc.), according to the purpose of the application. Following annealing at a Rockwell hardness of 38–42 HRC, the alloys have good machining properties and, after hardening, reach a Rockwell hardness of 68–71 HRC.

In parallel to melt-metallurgy, at the start of the twentieth century the first attempts were also made with the then new process of powder metallurgy to manufacture molds of tungsten carbide. The decisive break-through came in 1923, when K. Schröter of the Osram Studiengesellschaft mixed WC mono-carbide powder with 5–10 wt% Co, and then sintered the mixture at close to the melting temperature of Co. The (until then) unequaled strength values of the cemented carbide enabled their use for machining. Following purchase of the patent, the Krupp company launched the new cutting material on the market in 1925, under the name Widia ("wie Diamant"). Initially, this permitted the machining of cast alloys with a vastly improved performance, although only slight improvements were possible for the machining of steel, due to the high crater wear rate of the pure WC–Co cemented carbides. This problem was caused by the solubility of WC in the metals of the iron group (Fe, Ni, Co), and is the reason why WC may also be slightly attacked by the hot chips produced. Today, pure WC–Co compounds find application as thermal-spray wear protection coatings in many tribological applications (see also Section 6.2.6)

Between 1925 and 1931, under the direction of P. Schwarzkopf of the Metallwerk Plansee in Austria, crater wear-resistant cemented carbides were successfully developed with the introduction of carbides of the systems WC/TiC, Mo_2C/TiC, WC/Mo_2C, and also of the use of nickel as a bonding material, whereby sintering had to take place in a vacuum furnace. Parallel to this, in the USA, Fansteel introduced to the market (in 1930) a cemented carbide on the basis of TaC and Ni, while and in Germany Holzberger developed cemented carbides containing TiC, for which the Böhler company later acquired the rights. These new mixed-carbide-content cemented carbide types also brought about a veritable revolution of the cutting parameters that could be realized for the machining of steel that, above all, could be attributed to the formation of protective oxide layers on cemented carbides containing TiC and TaC. From 1934 onwards, cemented carbides with mixed carbides were marketed by virtually all manufacturers, whereby the cobalt-bound cemented carbide types on the basis of the ternary mixed carbides WC/TiC/TaC established themselves. Both, TaC

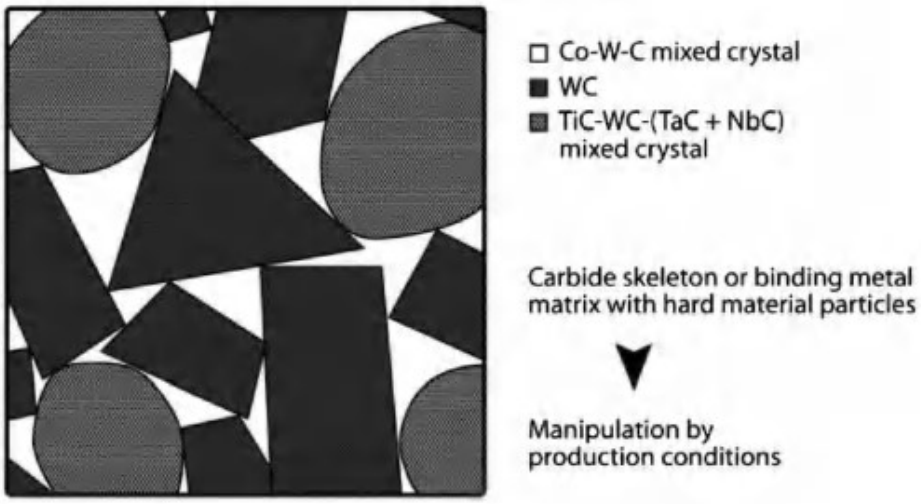


Figure 5.24 Schematic representation of a cemented carbide microstructure.

and small amounts of NbC or VC, were shown to inhibit grain growth in these types and, indeed, to this day WC–TiC–Ta/NbC–Co cemented carbides constitute the prevailing cemented carbide types for the machining of steel (Figure 5.24). The range of their use was further extended during the 1970s, with the introduction of high TaC contents, which improved their thermal cycling strength and therefore also allowed milling. Not only VC and Cr_3C_2, but also Ta/NbC, find application as grain growth-inhibiting additives in WC–Co cemented carbides. Cr_3C_2 also serves as a basis for special corrosion-resistant cemented carbide alloys. The properties of Mo_2C are similar to those of WC, to a point where Mo_2C has repeatedly been proposed as a partial substitute for WC. Molybdenum has also taken on great importance as an additive in tungsten-free, TiC-based cutting alloys.

The first cutting materials on the basis of TiC–Mo_2C–Ni (titanite S) were developed by P. Schwarzkopf at Plansee due to the patent situation, and marketed from 1934 onwards [54]. Due to the better solubility of TiC in Ni, Ni is preferably employed as a bonding metal. In Germany, following the Second World War, the lack of raw materials led to a resumption in the development of low-tungsten content cemented carbides, with TiC/VC–Ni(Fe) alloys showing good results. Interest was also resumed in TiC–Mo_2C–Ni cemented carbides, such that between 1950 and 1960 the alloying of bonding metals with molybdenum improved to the extent that cutting materials became as important as the Al_2O_3-based ceramics of the time, and indeed they are still in use today for certain applications. From the mid-1970s onwards, Rudy and colleagues developed very fine-grained, low-tungsten content cemented carbides with improved usage properties, by utilizing the spinodal decay of hard material components in the system Ti(C,N)–Mo(W)–Ni(Co). These (in part) low-tungsten-content cemented carbides contain nitrogen, and are known as "cermets" in technical terms; the term, which originated from the words "ceramics" and "metals," has led to composite metal–ceramic components acquiring a whole new meaning.

In addition to alloy-engineering measures, process-technical innovations have – since the 1970s – become increasingly important in connection with improvements