# 1
# Introduction

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## 1.1
### The Importance of Alloys at the Beginning of the Third Millennium

An alloy is a ''mixture'' of two or more chemical elements, one of which at least is a metal. The alloying element can be distributed over the crystal lattice sites of the host element and yield a solid solution, or it can form different phases showing up as particles in a ''matrix.'' Whereas the physical properties of a solid solution are essentially determined by the chemical composition of the constituents, the properties of a multiphase alloy are determined largely by the spatial distribution of the second-phase particles. This possibility of ''designing'' physical and technical properties of a material by a careful selection of alloying elements and alloying concentrations put alloys in the forefront of materials from early human history up to our time at the beginning of the third millennium.

We are facing tremendous progress in materials development and design of advanced materials, driven by technical needs in all fields of modern production. A real revolution in materials science, however, could be observed during very recent years, a great leap from understanding bulk materials to the study, development, and application of nanostructured materials. In the present book we give accounts of the state-of-the-art of alloy physics and the challenges of future research in the field together with the basic knowledge necessary to understand the radical changes currently happening.

Materials today, aside from metals and alloys, include such different substances as ceramics, high-$T_c$ (HT$_c$) superconductors, liquid crystals, polymers, foams, biomimetic materials, nanotubes, nanocomposites ... and it is justified to ask: ''What is the importance of *alloys* in the field of modern materials today? What role do *alloys* play in the fascinating advance toward nanostructurization?''

We will later cast a glance at the historical perspectives together with a short description of the development of modern alloy science. However, let us get started by affirming the importance of alloys at the onset of the third millennium.

**Conductors and superconductors**    In July 1996 overloaded transmission lines sagging low enough to touch trees caused a blackout of electric power which affected millions of people in the western part of the United States, Canada, and parts of Mexico. The blackout on August 14 2003 was the biggest in US history. Roughly 50 million people lost power due to a failure in the ''Lake Erie Loop.'' A similar event occurred in Europe on September 29 of the same year: some 57 million people lost their electrical power in Italy at the weekend when the national grid crashed. The minor event that a single tree fell across a line in the Alps during a storm started a domino effect which soon knocked out the entire Italian grid.

A key step in the process of improving the distribution of electric power lies in reducing the weight/conductivity ratio of utility transmission and distribution lines.

Aside from conventional conductors used for overhead transmission and distribution lines, special systems making use of superconductivity may be applied. The capacity of superconducting materials to handle large currents with no resistance and extremely low energy losses can be applied to electric devices such as motors and generators as well as to transmission in electric power lines. A superconducting power system would meet the growing demand for electricity with fewer power plants and transmission lines than was otherwise needed. High-temperature superconductors which need cooling to only about 80 K seem especially promising and are just about to enter economical use for utility applications. Possible applications are cables which carry up to five times more power than conventional utility cables, smaller and more efficient motors, smaller and lighter generators, compact transformers without oil (but with liquid nitrogen) as the cooling medium, fault-current limiters, and superconducting magnetic energy storage (SMES) systems which store energy in a magnetic field created by the flow of direct current in a coil of superconducting material.

**Soft and hard magnets**    Tailoring the ferromagnetic hysteresis curves is an ongoing demand in the field of soft and hard magnets. At one end of the spectrum magnetically soft materials reduce hysteresis losses, where necessary. Amorphous alloys, for example, show a high permeability and very low losses (especially low losses at elevated frequencies), but also a high magnetization at room temperature. At the other end, using rare earth alloys we get very high values of magnetization which have been increasing exponentially during recent years. Magnetically hard materials with high coercivity are needed for magnetic storage. To increase information storage density, nanosized magnetic domain structures are being developed. Nanocrystalline soft magnetic materials are already commercially available. Nanocrystalline hard magnetic materials exhibit interesting properties; an industrial breakthrough has not yet been achieved, however.

**Intermetallics and superalloys**    Intermetallic compounds, because of their long-range ordered structure, show a temperature range where their mechanical strength increases with temperature (yield stress anomaly). Together with their advantageous corrosion properties this selects them as potential high-

temperature structural materials. The present challenge is to combine extreme strength and hardness with sufficient ductility and surface stability, a problem which is not yet really solved.

At present, turbo superchargers and aircraft turbine engines are made of two-phase nickel-based superalloys, usually strengthened by a coherent precipitation of L1$_2$ ordered $\gamma'$ particles in the disordered face-centered cubic $\gamma$ matrix. The operating surface temperatures of turbine blades are close to 1150 °C, and the average bulk metal temperature approaches 1000 °C. Ni-based superalloys are also used in load-bearing structures at up to 90% of their melting temperature.

Another possible use of intermetallics when they are ferromagnetic and nano-structured is that for high-density magnetic recording, a field in which much effort is invested at the moment, especially in order to overcome the superparamagnetic limit.

**Shape memory alloys** These are alloys which exhibit thermoelastic effects and revert to the original shape by a phase transformation when they are heated after a plastic deformation. The applications of shape memory alloys are essentially in electrical/mechanical junctions, actuators which are the most promising alternatives to hydraulic systems, actuators for microelectromechanical systems (MEMS), surgical tools such as NiTi bone plates which apply a steady pressure to assist the healing process and thus reduce recovery time, and robotic muscles (shape memory alloys mimic human muscles and tendons very well). In addition, magnetic shape memory alloys (MSM) based on NiMnGa exist in which the martensitic transition can be triggered by an external magnetic field. These are alloys for which many applications can be expected.

**Nanocrystalline and amorphous alloys** Glassy forms of metallic alloys have quite unique mechanical, electrical, and magnetic properties. It has been found in the recent past that for certain alloy compositions appropriate cooling rates can be applied to form ''bulk amorphous alloys.'' Many of these alloys have a very high strength to weight ratio with excellent elastic energy storage. Other applications are in ferromagnets ranging from the lowest known coercivities to extremely high coercivities with high saturation induction values, as well as in composites made of ferromagnetic and antiferromagnetic components (giant magneto resistance), and in magnetic reading heads.

**Dimensionally restricted alloys** Dimensionally restricted systems are currently very fashionable in physics and materials science and research in this area easily attracts funding. In electronics, for example, the ever greater complexity in microprocessor and memory chips means an exponentially increasing chip density (with a doubling rate about two years at the moment: Moore's law). Individual electronic components are therefore smaller than 100 nm, bringing these conducting elements into the low-dimensional regime. Another field where nano-structurization commends itself is high-density data storage and magnetic or magneto-optic recording. Further materials enhancement is achieved by incorpo-

rating nanocrystalline particles to increase toughness or to improve catalyst properties.

In addition, there is a steadily growing general interest in the basic physics of low-dimensional alloys. Significant differences are obtained in the physical properties of nanosized structures as compared to the bulk, for instance a change in melting temperature or modification of microstructures. The changes in diffusion processes seem to be essential but are not known in detail. Other fundamental questions are which structural defects are stable and what their role is in phase transformations. It is therefore important to study all the changes which occur when going from bulk to thin films, nanowires, or small atom clusters.

**Friction and wear**  The reduction of friction between moving parts becomes more and more important for future mechanical applications, especially in modern combustion engines. On the one hand there are efforts to minimize the energy loss during operation; on the other hand there is the trend to simultaneously maximize the output and minimize the engine volume, in this way increasing the efficiency of engines. Friction properties and the resistance to high thermal stresses therefore become main design factors. Besides low friction and low wear rate, the materials must also have high fatigue strength and good ductility to sustain the deformation of the different parts caused by the firing pressure and by the inertial forces. To close the gap between the performance of conventional materials and the needs of the engines of the next generation, there is a very acute demand in alloy design for the design of new tribological alloys.

**Medical and biological applications**  Special alloy products are frequently used for medical applications, e.g. in accident surgery. Typically, these include orthopedic and dental implants, fracture fixation devices, suture needles and staples, surgical blades and saw cutting tools, dental burrs and reamers, catheter guide wire systems and wire for diagnostic and sensor electrical leads. Another area of current interest is biomimetic engineering. Inspired by Nature, biomimetic engineering copies natural systems, utilizing molecular self-assembly as the key link between physics, chemistry, and biology, and thereby creating novel advanced structures. The driving force stems from the recognition that there are a number of areas where biological methods are more efficient and environmentally friendly than current technology, and superior to it overall. These areas are, for example, energy storage and utilization, low-temperature fabrication of complex materials, linear motors and actuators, dirt-repellent surfaces, neural computation, sensors, and many other possible applications. Alloys play a major role in this field.

In conclusion, alloy physics is at the hub of materials science and materials physics. It turns out that virtually all high-technology developments are involving modern alloys, and alloy design is a driving force of scientific research in materials physics. This means that within the field of technological applications specialized alloys are involved in all cutting-edge technologies. In addition, alloys have essential repercussions in other fields as well, such as environmental tech-

nology to limit the growing ecocide, modern surgery and health care, and even the social and economic development of underdeveloped regions.

## 1.2
## Historical Development

### 1.2.1
### Historical Perspective

Modern anthropology dates the rise of the genus "human" at more than three million years ago (*Homo rudolfensis* and *Homo habilis*, both being potential ancestors of *Homo ergaster*, who thrived about 1.5 million years ago). Looking into the early history of man, certain development "steps" can be distinguished, which are correlated with a "revolutionary" advance of skills. One example is the first handling of fire in the middle of the Pleistocene (the Ice Ages) together with the manufacture of stone tools. This age is therefore also called the Old Stone Age (the Paleolithic period) and marks the first appearance of human species closely resembling ourselves (*Homo ergaster* → *Homo heidelbergensis* → *Homo sapiens*). It is certainly at that moment that "matter" changed into "material" – in the sense that a material is matter with some special use. Another "revolutionary" change led directly to the class of materials which is the focus of this book: The development of metallic alloys had probably started already in the Far East, in China and Indochina, Thailand, Vietnam, and East India before 5000 BC. Among the oldest known tin bronzes are the dagger of Veľke Raškovce in central Europe (Slovakia), containing 4.5 wt.% tin from the second half of the fifth millennium BC and pieces from Mundigak, Afghanistan, from the second half of the fourth millennium BC (Trnka 2006). The reason why those processes of human development look fast and "revolutionary" to us, while they are in fact slow and evolutionary, is to be found in the large timescale for counting these developments in the far past. Actually, a drastic reduction of the periods in which such far-reaching changes took place can already be recognized by comparing the Stone Age with the Bronze Age. Whereas the human development during the Stone Age took roughly a million years, the Bronze Age in Middle Europe was superseded by the Iron Age after no more than about 2000 years. A corresponding acceleration in technical development continues into present times, the replacement of electron tubes by transistors after only 50 years being such an example.

It is known that in early history the extended use of tools and weapons was essential for the survival of the human species, in the permanent search for food and in the fight against animals as well as other human species. Tools and weapons were first found accidentally in the near surroundings, then later made artificially from specific materials. This documents the importance of materials for mankind, which has continued right up to the 21st century. Very early in human history, alloys started to play a central role among the materials used, because it

was quickly recognized that many of the desired properties can be created by deliberately "mixing" together a metal with other components, especially other metals. Metal alloys, therefore, immediately started a new era of human life when tools of copper bronze (70–95% copper and 30–5% tin) prevailed over earlier ones made from stone or pure copper. The evolution of hardening a metal by alloying was accompanied by the possibility of casting complicated shapes in special molds made of wax embedded in clay.

We will now give an overview of the historical perspectives of alloys, followed by a short description of the development of modern alloy science.

During the final period of the Stone Age men became settled and started to live together in small tribes and communities. Lumps of native copper and later of gold collected from ice-free mountains and out of rivers, respectively, were probably the first metals to be discovered and both were immediately recognized as being excellently suited to substitute wood and bone in artwork. The first use of copper dates back more than 10 000 years (Ergani Maden and Catal Hüyük in the highlands of Anatolia). An intensified search then probably brought to light the bright green malachite and the blue azurite. It was learned that copper got hard when hammered and could be softened again by heating it. Early smelting techniques were already being applied around 6500 BC, first in East Asia (China) and West Asia (Near East), and from the first half of the fifth millennium BC onward in Europe also.

The very first bronze pieces used were made from "arsenic bronze," arsenic accidentally contained in the copper ore. It turned out to be easier to cast, more ductile, and harder than pure copper. It is now known that arsenic deoxidizes the harmful oxygen and thereby reduces brittleness. Later, by intentional addition of tin to copper, true "bronze" (tin bronze) was made and the production became independent of deposits with special ore. Its use spread very rapidly out of Mesopotamia to the Mediterranean countries, where bronze lasted for over 2000 years and even longer in north-western Europe (see Fig. 1.1).

It is assumed that the knowledge about iron smelting and how to obtain steel was first gained in the highlands of Anatolia where the Hittites flourished from about 1450 to 1200 BC, but several objects of smelted iron date back further than 2000 BC (Cowen 2005). When Tutankhamen was buried in about 1400 BC he had with him an iron dagger with a hilt and sheath of gold decorated with rock crystal. Surprisingly enough, the dagger blade had not rusted within the 3000 years and more until its discovery, whereas many other ancient iron objects probably perished as they were transformed into shapeless rust. Since the element iron practically always occurs as a compound, usually siderite ($FeCO_3$) and often together with malachite ($CuCO_3$), most of these very old iron weapons have been made from meteoritic iron or from the black sands on the south coast of the Black Sea containing the iron-rich magnetite ($Fe_3O_4$). One of the oldest known furnaces for "cooking" iron from iron ore are from Tell Hammeh, on the north bank of the Zarqa River in Jordan, and date to the eighth century BC (Veldhuijzen and Van der Steen, 2000). In Europe iron came into use with the development of iron smelting and working which began around 800 BC during the

(a)



(b)

**Fig. 1.1** (a) ''Strettweger Kultwagen,'' a beautifully made artefact showing a sacrificial procession with a cart, bearing a vessel containing some liquid for offerings. It was produced about 600 BC and found in 1851 near Judenburg, Austria (Egg 1996). (b) ''Kultwagen von Acholshausen,'' made about 1000 BC, found near Acholshausen, Germany (Worschech 1977/78). Both objects show the importance of coaches with spoke wheels as prestigious objects used for religious ceremonies.

Hallstatt culture, named after the famous cemetery near a salt mine at Hallstatt, Austria.

The usual way to obtain useful products from the unattractive, unmelted iron which is left in the furnace (a spongy mass, the ''bloom'', containing slag) is to hammer the liquid slag out of the hot lump, yielding fairly pure wrought iron. The result may not be better than bronze. Only in a forging process with a long procedure of hammering and reheating were superior steels obtained. In charcoal-fired forges the fresh, hot surface of the wrought iron comes into contact with carbon and carbon monoxide which thus ''carburize'' the iron surface to form steel as an iron–carbon alloy.

Alloying iron with more than 2% carbon considerably reduces the melting temperature with respect to iron and makes it possible to cast in molds. Whereas in the western hemisphere this development was discouraged by the knowledge that more than 1% carbon makes the iron alloy brittle, the superior furnace technology in China already allowed iron casting in the first half of the first millennium BC, and the technique of decarburization by reheating to 800–900 °C in air between 400 and 300 BC (Cowen 2005).

When they came to the Near East during the Crusades, European knights learned to fear the extreme quality of razor-sharp Damascene blades (see Fig. 1.2). Two production methods have been applied, both dating back to before 500 AD. One method was to forge two ingots of high- and low-carbon steels, respectively, into flat sheets and after cutting them to pieces, intimately bonding the

(a)                                                                                     (b)
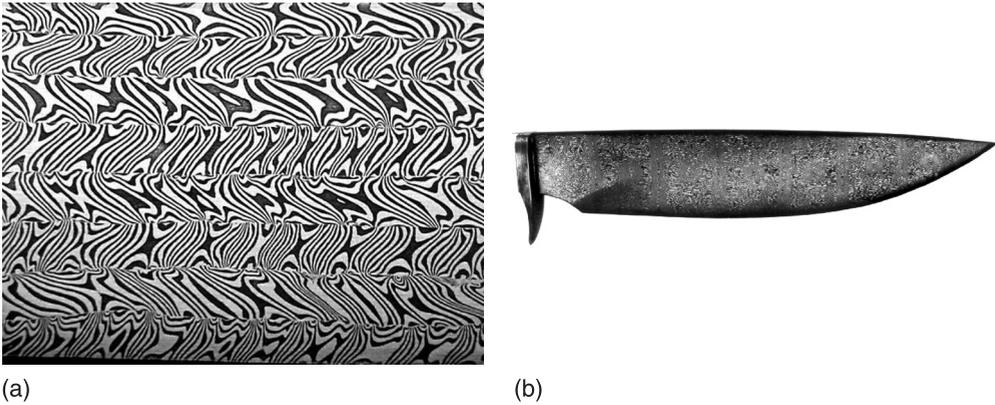
**Fig. 1.2** (a) Etched surface of a Damascus blade showing in detail the
Damascene surface pattern generated by continued folding and twisting
during forge welding of alternating sheets of high- and low-carbon
steels. (b) A reconstructed Damascus blade showing the Damascene
surface pattern (''Mohammed's ladders'' and ''rose patterns'')
produced from a single wootz steel ingot (Verhoeven et al. 1998).
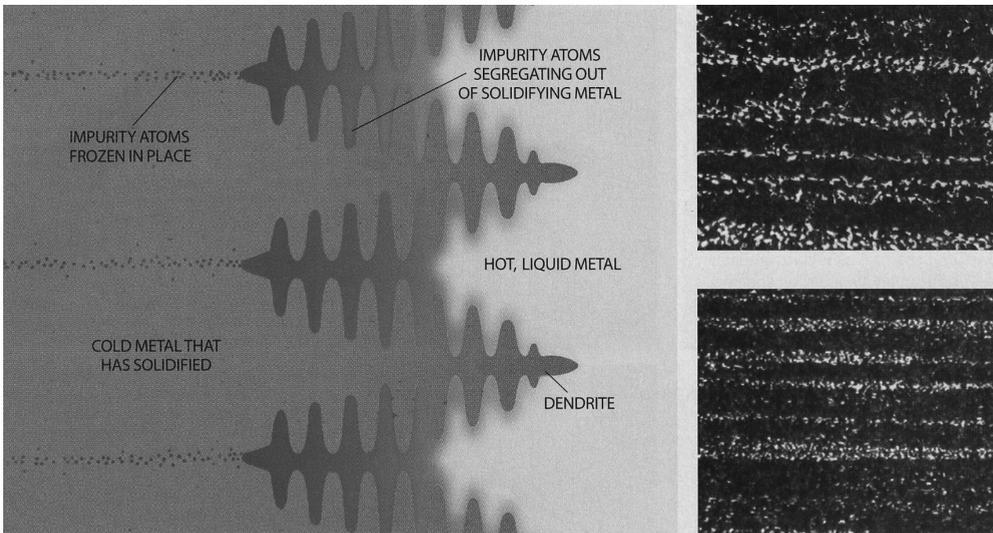


**Fig. 1.3** During cooling of the ''wootz'' ingot, impurity elements (e.g.
vanadium) segregate out of the solid iron and freeze in an aligned way.
Subsequent cycles of heating and cooling lead to a growth of iron
carbide particles ($Fe_3C$, cementite) along the lines, forming the light-
colored bands in the Damascene blade. Right: Micrograph showing
light and dark bands in an original Damascene blade (top) and a
modern reconstruction (bottom) (Verhoeven 2001).

pieces together by continued folding, twisting, and hammering the work piece (Fig. 1.2a). The other method started from a single high-carbon steel ingot, called ''wootz'', originally produced from special ore in India. The wootz was then forged in many heating–cooling cycles (Fig. 1.2b).

The secret of the production of Damascene blades from a wootz steel ingot was unfortunately lost during the 18th century, but has recently been rediscovered in a co-operation between a scientist and a blacksmith (Verhoeven et al. 1998; Verhoeven 2001). It turned out that the surface patterns on the blades resulted from the formation of bands of iron carbide ($Fe_3C$) particles initiated by the microsegregation of carbide-forming impurity elements being present in the wootz ingots (Fig. 1.3).

### 1.2.2
### The Development of Modern Alloy Science

Whereas, as we have seen, the roots of alloy production go back into early human history, what we can call ''scientific alloy research'' started in the 19th century. It is well known that the 19th century was very productive in several fields; the time of the industrial revolution was accompanied by a deep belief in progress and in universal feasibility, and several new branches of science (social, medical, biological, technical) were developed. The progress in science and technology began to be tightly connected. The foundations were laid for more sophisticated studies of alloys by the development of crystallography, elasticity, electrochemistry, and metallography, together with a parallel advance in experimental methods (e.g., thermometry and measurement of electrical resistivity and hardness).

In his two articles ''On the Equilibrium of Heterogeneous Substances'' (in 1876 and 1878, respectively), J. W. Gibbs applied thermodynamics to the phase equilibria of alloys, introduced the phase diagram as a basis of modern alloy science, and derived his famous phase rule. We can indeed connect the rise of modern alloy physics with this pivotal work of Gibbs. An important first step toward an understanding of alloy kinetics was the investigation of solid-state diffusion by W.C. Roberts-Austen, showing in 1896 that the diffusion coefficient of gold in lead was surprisingly far greater than supposed. The systematic study of binary phase diagrams is closely connected with G. Tammann. Generations of students used Tammann's famous book *Lehrbuch der Metallographie* (first published in 1914) for getting started with binary phase diagrams. The idea of the crystallinity of metals and alloys was already growing during the 18th and 19th centuries, but conclusive evidence of their crystalline structure was furnished after the discovery of X-rays as electromagnetic waves which could be diffracted by crystals (M. von Laue in 1912). Immediately afterward, W. H. Bragg and his son W. L. Bragg used X-rays systematically for the study of crystal structures (in 1913–1914). The determination of crystal unit cells of many primary and intermediate phases brought about a real revolution. This was also the onset of the study of chemical long-range order (LRO), i.e., the condensation of the different sorts of atom in an alloy on specific sublattices of the crystal structure. The three papers by W. L. Bragg

and E. J. Williams discussed for the first time the degree of LRO and LRO kinetics with respect to atomic interaction energies (Bragg and Williams 1934, 1935; Williams 1935). These papers are still great reading for anybody entering the field of ordering kinetics.

In 1930, F. Laves tried a classification of crystal structures from a topological point of view and found special compounds which are stabilized by their high packing density. These ''Laves phases'' have a packing density higher than a close-packed structure of identical hard spheres.

Besides phase diagrams, Tammann investigated extensively the mechanisms of phase transformations during freezing, which led to the development of a theory of nucleation by M. Volmer and A. Weber in 1926, later applied to solid-state phase transformations by R. Becker and W. Döring (in 1935).

In 1926 W. Hume-Rothery showed that the electron/atom ratio plays a decisive role in the determination of the solid solubility of copper, silver, and gold alloys with B-subgroup metals and also for the so-called ''magic numbers'' of concentrations involved in the intermediate phases of these alloys. The reason lies in variations of the band structure for different crystallographic systems which comes into play when metals of different electron/atom ratio are alloyed together.

Much effort within physical metallurgy and alloy physics has of course been put into the study of plastic deformation. Great progress in this respect was the possibility of growing single crystals (J. Czochralski in 1917; P.W. Bridgman in 1925), allowing the investigation of plasticity without any influence of grain boundaries and with a well-defined orientation. The fundamental studies of M. Polanyi, E. Schmid, and W. M. Boas were summarized in the famous book by Schmid and Boas in 1935 establishing the critical resolved shear stress as a fundamental criterion for slip. In this macroscopic description of plasticity, a fundamental problem remained unsolved: The experimentally observed yield stress of single crystals is several orders of magnitude lower than calculated from the theoretical strength determined for the rigid glide of lattice planes. This led to the postulation of dislocations by M. Polanyi, E. Orowan, and G. I. Taylor (separately, in 1934), which later, after a further development of the electron microscope by E. Ruska (in 1931), was brilliantly confirmed by transmission electron microscopy (TEM) of thin crystals by Heidenreich (in 1949) and P. B. Hirsch (in 1954).

J. Frenkel (in 1926) and C. Wagner, as well as W. Schottky (in 1930), postulated point defects, vacancies, and interstitials as very important for the physical properties of metals and alloys. Vacancies turned out to be essential for diffusion, as was shown theoretically by H. B. Huntington and F. Seitz in 1942, later confirmed experimentally as fact by A. D. Smigelskas and E. O. Kirkendall (in 1947), and critically analyzed by L. S. Darken (in 1948). The Kirkendall effect of marker movement during chemical diffusion of two components with different diffusion coefficients is generally accepted as evidence for the vacancy diffusion mechanism.

The theory of phase transformations in alloys, originally dominated mainly by the nucleation and growth concept, was greatly developed by efforts to explain superconductivity (H. Kamerlingh-Onnes in 1911) and superfluidity (P. L. Kapitsa, J. F. Allen, and D. Misener in 1937). First a concept was developed on a phenom-

enological level by L. D. Landau in 1938 to explain second-order phase transitions, but it applies to more general physical transition problems (see, e.g., Melbourne 2000). Another essential development reaches back to Gibbs and Volmer: spinodal decomposition, with the consequence of ''uphill'' diffusion. The problem was described theoretically by J. W. Cahn and J. E. Hilliard in 1958 in a continuum approach and by M. Hillert (in 1961; and also in his 1956 thesis) in an atomistic approach. Corroboration came from small-angle scattering experiments in the early stages of decomposing systems (see, e.g., Gerold and Kostorz (1978), for a first review on this matter). An atomistic approach to obtain theoretically phase diagrams and information on the kinetics of phase transformations from statistical thermodynamics was developed in 1950 by R. Kikuchi, called cluster variation method (CVM), and was later extended to the path probability method (PPM) for describing transformation kinetics (in 1966). In 1949 N. Metropolis and S. Ulam first described the Monte Carlo method (MC) of random variations of the microstate; today it is one of the leading methods in alloy physics for studying structure and kinetics.

After C. J. Davisson and L. H. Germer in 1927 had observed the wave character of electrons in diffraction experiments on Ni crystals, it was only a small step to scattering experiments with neutrons, yielding phonon dispersion curves, diffuse scattering, and magnetic scattering with polarized neutrons.

The density functional theory (DFT) by P. Hohenberg and W. Kohn (in 1964) and W. Kohn and L. J. Sham (in 1965) solved the fundamental problem of many-body interactions in a solid. It was therefore a starting point for a quantum mechanical ab-initio approach to realistic phase diagrams and materials parameters. The theory has been very successful in recent years at describing the ground-state properties of metals and alloys. Very recently the DFT was combined with statistical thermodynamics within the cluster expansion method (CEM) by J. M. Sanchez, F. Ducastelle, and D. Gratias (in 1984). When this is applied together with MC simulations, a *quantitative* study of alloy properties is also made possible with respect to the temperature dependence.

The work of Cahn and Hilliard, and later S. M. Allen and J. W. Cahn (in 1979), laid the basis for a general modeling of multiphase systems, called phase field modeling (PFM), which has been used successfully to study solidification and phase transformation in alloys.

Since the mid-1990s, electron microscopy as well as field ion microscopy, originally invented by E. W. Müller in 1951, made a big advance. Methods for electron microscopy were developed to obtain atomic resolution (high-resolution TEM, or HRTEM) by special observation techniques and technical correction of aberrations. The original field ion microscope and its analytical version, the atom probe, have recently been upgraded to 3D tomography atom probe (A. Cerezo in 1988; D. Blavette in 1993): The field-evaporated part of a very fine tip is simultaneously imaged on a position-sensitive detector and chemically analyzed by a time-of-flight (TOF) measurement. If all data are carefully stored as a function of time, the sample can be computer-reconstructed on an atomic scale. The development of scanning probes for atomic-scale microscopy led to further extremely fruitful experimental tools: the scanning tunneling microscope (STM) invented by G.

Binning and H. Rohrer in 1982, and the atomic force microscope (AFM) by C. F. Quate, G. Binning, and C. Gerber in 1985. Using a cantilever with magnetic coating enables the AFM to be extended to the study of magnetic structures as the magnetic force microscope (MFM).

Since their use in historical times, alloys have never left the front row of advanced materials. Among the greatest challenges of alloy physics today are the following topics:

- ductile, high-temperature, high-strength, structural materials
- high-density, magnetic and magneto-optic, recording media
- physical behavior with restricted dimensions
- alloy behavior under extreme conditions
- increasingly accurate computation of physical parameters, especially by ab-initio calculations
- access to alloy kinetics by PPM, PFM, molecular dynamics (MD), and MC simulations supported by CEM.

Having at hand elaborate experimental and theoretical methods together with the possibility of computer simulations, further developments in the field of advanced alloys and alloy design will continue to contribute to the overall scientific and technological progress.

## 1.3
## Atom Kinetics

As we have seen already in the historical perspective, producing an alloy with specific properties has always needed specific microstructural changes, such as take place in the carburizing process when forging iron in the flame to get steel or in the special segregation processes for the famous Damascene blades. It is absolutely clear that all diffusive structural changes in a crystal are ultimately brought about by atoms jumping between different lattice sites. If atoms are not able to move, no change at all is possible and the alloy remains frozen in the current state. For physical properties of an alloy to be meaningful they have to be measured in a thermodynamic equilibrium state. The knowledge of atom jump processes is an essential prerequisite to decide if the system is in a true equilibrium state. Furthermore, detailed information on alloy kinetics is required for the design and development of advanced alloys.

Some examples will underline the importance of atom jumps for alloy physics. During the solidification process the homogeneity/heterogeneity/crystallinity of the solid alloy is almost completely determined by atomic mobility. Fast cooling of the melt, for instance, enables the production of metallic glasses with alloy properties far different from crystalline materials.

Dislocation reactions essentially determining the mechanical properties are widely influenced by atom jump processes bringing about the motion of vacancies and solute atoms.

Atom jumps, mainly into neighboring vacancies, are the underlying mechanism of nondisplacive phase transformations. Therefore, what really happens depends critically on the local atomic motion in an alloy (see, e.g., Soffa et al. 2003).

Phase changes of the order–disorder type are of special interest due to their reversibility. In this case atom jumps occur between different sublattices of the ordered or at least partially ordered alloy. A fundamental understanding of the role of defects in intermetallic compounds can then be attempted, which will allow open questions on configurational kinetics of alloys to be answered.

We have further seen that size reduction to obtain nanostructures is a current challenge in alloy physics. Essential changes in physical properties of alloys accompany dimensional restrictions. These are due to the increase in surface/volume ratio so that the atom jump processes run in a different manner than those in bulk alloys.

The necessary information on atom jump processes may be obtained by a combination of experimental and theoretical methods, together with computer simulations (see, e.g., Pfeiler et al. 2004; Kozubski et al. 2004, 2006).

Because of their importance and ubiquity in all microstructural changes, both desired and unwanted, it was decided to choose ''atom jump processes'' as a guiding principle and leitmotiv through this book.

## 1.4
## The Structure of this Book

When one looks at the Contents pages, the structure of this book (or let's say the order parameter) will become apparent: from statics to dynamics and kinetics, from fundamental to complex structures, from phenomenology via theory and experiment to applications.

This section gives a short overview of the chapters and their interconnections.

Chapter 2, ''Crystal Structure and Chemical Bonding,'' is dedicated to a classification of structure types and the relationship between structures and structure-determining parameters. A modern view of Hume-Rothery alloys and intermetallic compounds is given as well as of Laves phases and structurally more complex alloy systems such as magnetic materials of the $CaCu_5$ type or quasicrystals.

Alloy structure and structural defects depend of course on the solidification process. In Chapter 3, ''Solidification and Grown-in Defects,'' it is shown how diffusion, mainly on the liquid side, and convection processes close to the solid–liquid interface determine details of the resulting alloy structure. The generation of defects, formation of grain structure, twinning, and chemical segregation effects are other topics in this chapter.

Starting from a discussion on atomic binding and atomic interaction energies, a review is given in Chapter 4, ''Lattice Statics and Lattice Dynamics,'' on the elasticity of crystalline lattices, lattice vibrations, and thermal properties of alloys. Examples are shown of soft phonon modes and their influence on structural phase transitions, and special emphasis is put on the connection of phonon spectra with

atomic migration, allowing a determination of migration energies from lattice-dynamical properties.

The importance of lattice defects for atomic migration plays a central role in Chapter 5, "Point Defects, Atom Jumps, and Diffusion." The discussion starts with point defects and their energetics in alloys and continues with the different descriptions of single and multiple atom jump processes leading to atomic diffusion under various conditions. There is a fairly detailed discussion of diffusion in ordered intermetallics and of various theoretical approaches to obtain the macroscopic diffusion behavior from atom kinetics.

Plastic deformation of alloys due to dislocation processes is reviewed in detail in Chapter 6, "Dislocations and Mechanical Properties." The mechanisms discussed include thermally activated processes such as dislocation glide and climb, as well as hardening and recovery, complex deformation behavior like the famous yield strength anomaly and fatigue, the strength of nanocrystalline alloys and thin layers, and the mechanical properties of quasi-crystals.

The mechanisms of phase transformations in alloys are reviewed in Chapter 7, "Phase Equilibria and Phase Transformation." After a solid introduction on phase diagrams, phase transformation kinetics is described, and how it can be suppressed to get amorphous alloys is dicussed. The difference between nucleation and growth on the one hand, and spinodal decomposition on the other, is discussed for the cases of phase separations as well as for order–disorder transformations. Martensitic transformations, which are massive and displacive, are presented at the end of this important chapter together with some applications.

Chapter 8, "Relaxation of Nonequilibrium Alloys," first concerns description of alloy relaxation to an equilibrium structure by diffusion-controlled, thermally activated processes, starting from a nonequilibrium state. It is shown that a realistic kinetic pathway can be found by linking the classical nucleation theory to the details of atomic jumps. Secondly driven alloys are considered, for which an external forcing maintains the alloy in nonequilibrium states. The theory and modeling of such alloys rests on the combination of kinetics: that resulting from the external forcing and that of natural relaxation to equilibrium.

In Chapter 9, "Change of Alloy Properties under Dimensional Restrictions," detailed studies of phase equilibrium and phase transformations of nanometer-sized alloy particles are presented and a discussion on atom movement in nano-particles is given. It is shown that a stable amorphous phase can form in a eutectic system for a small enough particle size (below 10 nm), which promises an insight into the liquid–glass transition.

The theoretical basis of Chapter 10, "Statistical Thermodynamics and Model Calculations," is the cluster variation method (CVM). The statistical thermodynamics on a discrete lattice and for continuous media are reviewed and it is shown that by combining the CVM with calculations of the total energy of the electronic structure, self-consistent first-principles calculations of phase equilibria are made possible. Results of calculations using CVM and PPM (the path probability method) are presented and a possible approach toward first-principles phase field calculations is discussed.

Chapter 11, "Ab-initio Methods and Applications," is dedicated to a review of the present state of density functional theory. After an account of the theoretical background, the different computational methods and approaches are discussed critically and several examples of applications are given, such as elastic and vibrational properties, point defects and diffusion, the search for ground-state structures, and ordering phenomena. It is shown that the very successful cluster expansion method yields access to multiscale modeling.

In Chapter 12, "Simulation Techniques," advantages and disadvantages of molecular dynamics simulations are discussed first and some interesting results are given. Then various Monte Carlo (MC) simulation techniques, including kinetic MC, are described, and their possibilities and limits are shown in several examples. In the final part of the chapter, phase field models are explained, starting from their principles. These models are used to describe, e.g., the precipitation of a new phase, grain growth in polycrystals, and solidification.

Two chapters on experimental methods focus on high-resolution techniques: Chapters 13.1, "High-Resolution Scattering Methods and Time-Resolved Diffraction," and 13.2, "High-Resolution Microscopy." To study nonequilibrium alloys or equilibrium dynamics a high temporal experimental resolution is of great interest, which can be met under certain conditions, especially using the third generation of synchrotron sources. In Chapter 13.1, examples are given of high-resolution X-ray and neutron scattering methods, which include magnetic scattering, coherent time-resolved scattering, elastic, quasielastic, and inelastic scattering as well as diffuse scattering and scattering from surfaces.

In Chapter 13.2, after a short introduction to the field of surface analysis by scanning probe microscopy, the basic principles and practical aspects of HRTEM and related techniques are provided. This is followed by several examples, particularly emphasizing the use of in-situ HRTEM. The second part of this chapter focuses on up-to-date atom probe tomography, giving a detailed description of the method. Exemplary studies are described on decomposition, diffusion in nanocrystalline thin films, and grain boundary diffusion.

Chapter 14, "Materials and Process Design," is dedicated to various applications of alloys, and tries to convey a sound understanding of the corresponding effects and their up-to-date technical uses. These include soft and hard magnetic materials, invar alloys, magnetic media for the use in hard disk memories, spintronic materials showing giant magnetoresistance, and phase change media which use the phase transformation from crystalline to amorphous state for data storage. Last but not least the story of superconductors is related.

It is clear that the chapters summarized above have multiple connections; some important concepts are discussed in several chapters from different aspects. An example is the formation of a new phase from a supersaturated matrix. This process, which is fundamental for alloys, is discussed from the viewpoint of atom jumps mediating the transformation process in Chapter 5, a description starting from the basics is presented in Chapter 7, a prospective theoretical modeling of the kinetic process is formulated in Chapter 8, changes in the transformation behavior under the dimensional restrictions of nanometer-sized particles are illus-

**Table 1.1** Key to the topics in this book.

| Topic | Introduction | Structure | Solidification | Lattice dynamics | Defects & diffusion | Mechanical properties | Phase transformations | Relaxation & driven alloys | Dimensional restrictions | Statistics & modelling | Ab-initio applications | Simulations | Scattering methods | HR microscopy | Design & applications |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Chapter no.: | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13.1 | 13.2 | 14 |
| Ab-initio | ○ | | | | ○ | ○ | | | | ○ | ● | ○ | | | ○ |
| Alloy design | ○ | | ○ | | ○ | ○ | ○ | ○ | | | ○ | | | | ● |
| Amorphous alloys | ○ | | ● | | ○ | | ○ | | ○ | | | | ○ | | ○ |
| Anisotropy | | ● | | ○ | | ○ | ○ | | | | ○ | | | | ○ |
| Atom jump | ○ | | ○ | ○ | ● | ○ | ○ | ○ | ○ | ○ | ○ | ○ | | | |
| Cahn–Hilliard | ○ | | | | ○ | | ○ | ○ | | ● | | ○ | | | |
| Cluster expansion | ○ | | | | ○ | | | | | ○ | ● | | | | |
| Cluster variation | ○ | | | | ○ | | ○ | | | ● | | | | | |
| Complex alloys | | ● | | | | ○ | | | | | ○ | | ○ | | ○ |
| Crystal structure | | ● | ○ | ○ | ○ | ○ | ○ | | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| Diffusion | ○ | | ○ | ○ | ● | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| Dislocations | | | ○ | | ○ | ● | ○ | | ○ | | ○ | | ○ | ○ | |
| Elasticity | | | | ● | | ○ | ○ | | | | ○ | | | | |
| Grain structure | | | ● | | ○ | ○ | ○ | | ○ | | ○ | ○ | ○ | ○ | ○ |
| HR microscopy | ○ | | | | | ○ | ○ | ○ | ○ | | | | | ● | |
| Inelastic scattering | | | | ○ | | | | | | | ○ | | ● | | |
| Interaction energies | ○ | ○ | ○ | ● | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | | |
| Interfaces | | | ○ | | ○ | ○ | ○ | | ○ | ○ | ○ | | ○ | ● | ○ |
| Intermetallics | ○ | ● | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| Jump barriers | | | | ○ | ● | | | ○ | | ○ | ○ | ○ | | | |
| Lattice dynamics | | | | ● | | | ○ | | | | ○ | | ○ | | |
| Liquid alloys | | ● | | | | | | | ○ | | | | ○ | | |
| Long-range order | ○ | ● | ○ | ○ | ○ | ○ | ○ | | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| Low-dimension | ○ | | | | ○ | ○ | | | ● | | ○ | ○ | ○ | ○ | ○ |

**Table 1.1** *(continued)*

| Topic / Chapter no.: | Introduction 1 | Structure 2 | Solidification 3 | Lattice dynamics 4 | Defects & diffusion 5 | Mechanical properties 6 | Phase transformations 7 | Relaxation & driven alloys 8 | Dimensional restrictions 9 | Statistics & modelling 10 | Ab-initio applications 11 | Simulations 12 | Scattering methods 13.1 | HR microscopy 13.2 | Design & applications 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Magnetism | ○ | | | | | | | | | | | ○ | ○ | | ● |
| Martensitic trafo | | | | ○ | | ○ | ● | | | | | | | ○ | |
| Master equation | | | | | ● | | ○ | ○ | | | | ○ | | | |
| MC simulation | ○ | | | ○ | ○ | | ○ | ○ | ○ | ○ | ○ | ● | ○ | ○ | |
| Metastability | ○ | ○ | ○ | | ○ | | ● | ○ | ○ | ○ | ○ | | | | |
| Molecular dynamics | | | | ○ | ○ | | | | | | ○ | ● | | | |
| Multi-scaling | | | ○ | | | | | | | ○ | ● | | | | |
| Phase field method | ○ | | ○ | | | | | | | ○ | | ● | | | |
| Phase transformation | ○ | ○ | ○ | ○ | ○ | ○ | ● | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| Phonons | | | | ● | | ○ | ○ | | | | | ○ | ○ | | |
| Plastic deformation | | | ○ | | | ● | ○ | ○ | | | | | | ○ | |
| Point defects | | | ○ | ○ | ● | ○ | ○ | ○ | ○ | | | ○ | ○ | ○ | |
| Precipitation | | | | | ○ | ○ | ● | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| Quasicrystals | | ● | | | | ○ | | | | | | | ○ | | |
| Recovery & recryst | | | | | | ● | ○ | | | | | | | ○ | |
| Scattering methods | | | | ○ | ○ | | ○ | ○ | | | | | ● | | |
| Short-range order | | | | | ○ | | ● | | | ○ | ○ | ○ | ○ | | |
| Solute–defect interface | | | | | ● | ○ | ○ | ○ | ○ | | | ○ | | | |
| Spinodal | | | | | ○ | | ○ | ○ | | ● | | ○ | ○ | ○ | |

● principal treatment of this topic, ○ minor treatment.

trated in Chapter 9, statistical models of phase transitions are presented in Chapter 10, the advantage of DFT together with the cluster expansion method and kinetic MC simulations is documented in Chapter 11, the application of phase field models is discussed in Chapter 12, the experimental access to details of phase transformations by high-resolution scattering techniques as well as by TEM and atom probe tomography is presented in Chapters 13.1 and 13.2, respectively, and finally, possibilities of technical applications, e.g., of the phase change media for data storage in CDs and DVDs, are described in Chapter 14. Table 1.1 shows how important topics figure in different chapters. It is our explicit intention to present these various aspects, instead of conscientiously avoiding any overlap. We hope that this many-sided approach makes this book even more attractive.

In the course of this introductory chapter, we have tried to demonstrate that alloys still have to be counted among the most important materials of the 21st century, especially when considering the ongoing shift in interest from bulk materials to nanostructures. It goes without saying that a thorough understanding of the physics of alloys is a precondition for anyone who wants to do serious research or to engage in technical application of alloys. The present book covers in much detail and considerable depth nearly all fields of alloy physics necessary to know when entering one of these areas either as a graduate student or post-doc. It should be valuable for scientists of neighboring fields or somebody already working in an area of alloy physics who wants more information in one of the specific directions covered by this compendium.

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