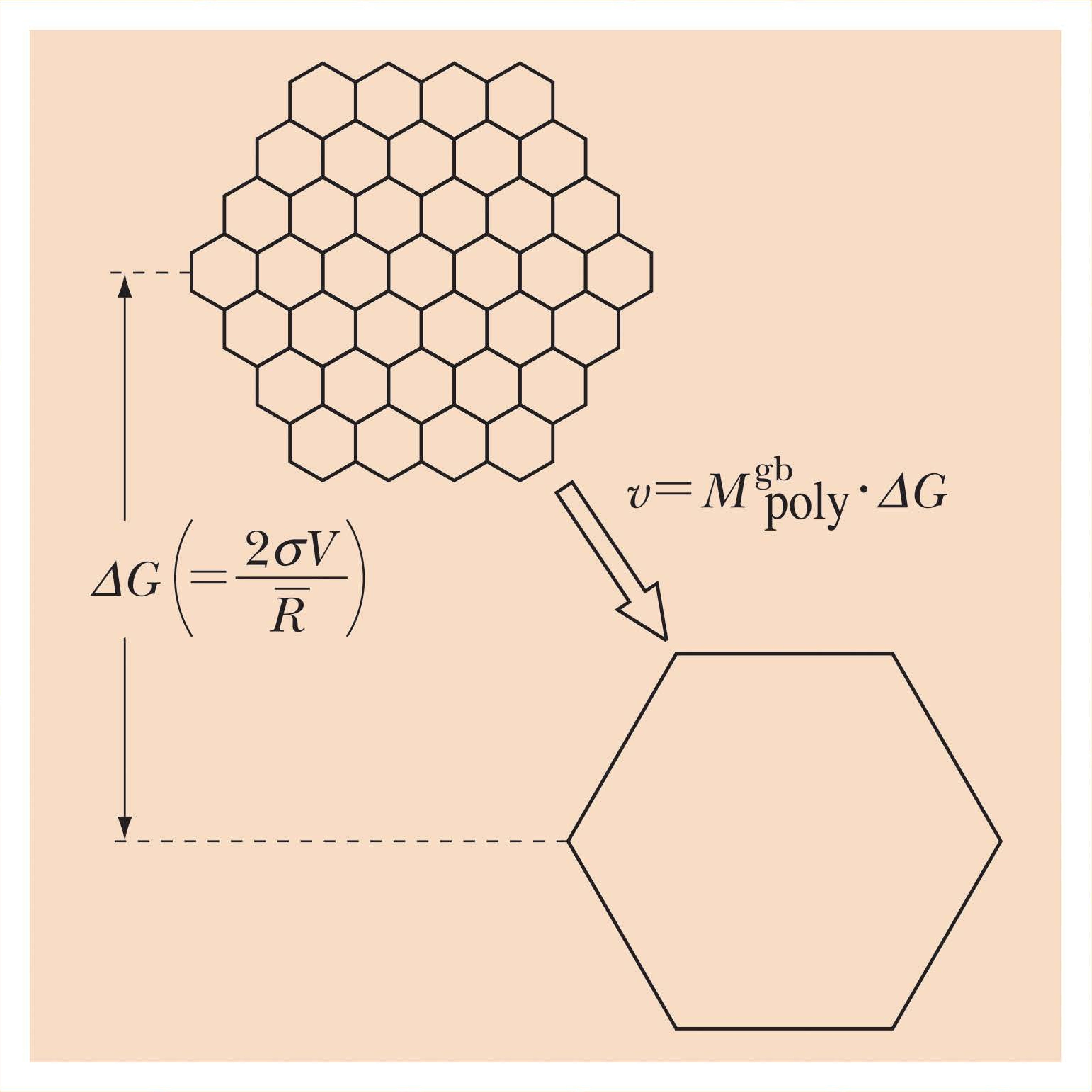
THERMODYNAMICS OF MICROSTRUCTURES

T. Nishizawa



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Thermodynamics of Microstructures

Taiji Nishizawa

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Preface

All the materials, both natural materials such as wood and artificial new materials, have their internal structures (or microstructures).

Development of the "microstructure" study started with the microscopic observation of iron and steel by H.C. Sorby (1863), and metallography was in advance until the 1950s. But since then, microscopic study on ceramics and polymers also made a great advance, and rapid progress has been made in materials science, which all-inclusively deals with these materials of various science branches.

The "microstructure" study is also on the other lineage descended from "thermodynamics of heterogeneous equilibria" founded by J.W. Gibbs (1875). Because thermodynamics is originally a branch of science whose subject matter is "control of heat and force" and it has invisible and abstract conceptions of such keywords as energy, entropy, chemical potential, and so on, it may be less familiar to the students who aim to engage in material development.

However, the time has already come when we not only can construct a phase diagram of multicomponent system called "a map of a material," but we can also predict change of microstructure such as "precipitation" or "eutectoid transformation" by computer calculation, and microscopic study cannot go without thermodynamics.

The title of this book was *The Structures of Materials* at first, but it has been changed to *Thermodynamics of Microstructures* in order to correspond to such an abrupt change of the situation. Moreover, this book avoids ordinary explanatory style, but adopts a Q&A style of exercises. This is because I think that it is much more effective in true comprehension of thermodynamics to practice actual examples than to learn fundamental laws by heart.

I hope this book will be a help to you as you work in material development.

This is the English version of the book published by the Japan Institute of Metals in 2005. I wish to express my sincere gratitude to ASM International, the Japan Institute of Metals, Prof. Kiyohito Ishida, Prof. Ikuo Ohnuma, Mr. Hiroyasu Takahashi, Mr. Akira Idogawa, Dr. Yoshimasa Kajiwara, and Mr. Charles Moosbrugger deeply for undertaking this publication.

Taiji Nishizawa
September 2008, Sendai

About the Author

Professor Taiji Nishizawa is Professor Emeritus at Tohoku University and an Advisor to Sumitomo Metal Industries, Ltd. He holds a B.Sc. and D. Eng. Degrees in Materials Science from Tohoku University, where he taught. He has also been a visiting researcher at the Royal Institute of Technology in Sweden.

Professor Nishizawa has served as Vice President, Iron and Steel Institute of Japan; President, Japan Institute of Metals; and more Chairman, Japanese Committee for Alloy Phase Diagrams. In addition to authoring more than 150 technical papers, he has been Associate Editor, Bulletin of Alloy Phase Diagrams; Associate Editor, Calphad; and Japanese Representative of Alloy Phase Diagram International Commission (APDIC).

A small selection of his many professional awards include Gibbs Triangle Award (1994), Honda Gold Medal Award (1998), Gold Medal, The Japan Institute of Metals (2001), Tawara Gold Medal, The Iron and Steel Institute of Japan (2005), and the Hume-Rothery Prize, Institute of Materials, Minerals & Mining (2007).

CHAPTER 1

Introduction—An Overview of Microstructure in Materials

It is only with the heart that one can see rightly;
what is essential is invisible to the eye.
—Antoine de Saint-Exupéry, *The Little Prince* (Katherine Woods translation)

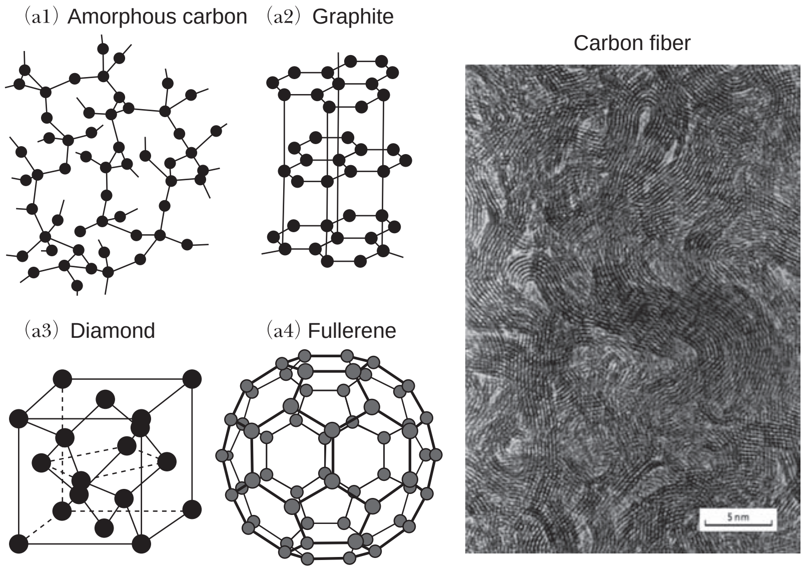
1.1 Matter and Materials

''What are materials?'' To address this question, let us first consider the difference between *materials* and *matter*. These words and the distinction between them have been defined in various ways. This book distinguishes *materials* from *matter* through the concept of *microstructure*.

For example, when asked about carbon, the element with the atomic number 6, scientists who are interested in the essence of matter may describe it in terms of its crystal structure, the binding forces between the atoms, and so on, imagining a diamond or fullerene structure (Fig. 1.1a). Engineers or researchers who are more concerned with applications of carbon may discuss it in terms of the strength of its microstructure, imaging the array of approximately 1 nm thick graphite crystalline ribbons in the carbon fibers used for tennis rackets or golf club shafts (Fig. 1.1b).

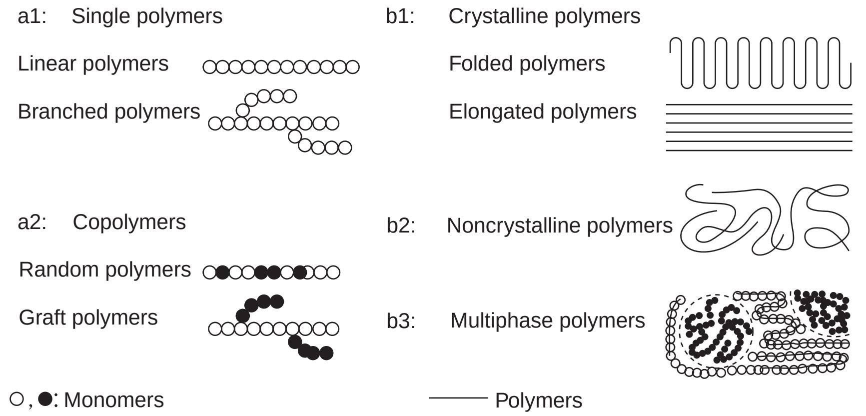
In the latter case, carbon is recognized as a *material*, with attributes defined by its *microstructure*. In the former case, on the other hand, carbon is recognized as *matter*, and absolutely perfect single crystals are the ideal objects for study because the principal purpose of investigation is the fundamental essence of the substance.

Now, as another example, consider macromolecules (polymers). Macromolecules are *matter* with linearly or reticularly combined unit molecules (i.e., monomers) consisting of 10^3 atoms or more; homopolymers consist of a single type of monomer, and copolymers consist of two or more types of monomers (Fig. 1.2a). Because most macromolecules are



(a) Matter **(b) Materials**

Fig. 1.1 The distinction between *matter* (characterized by structure) and *materials* (characterized by microstructure)



(a) The primary structures of polymers (molecular structures) **(b) The higher-order structures of polymers (microstructures)**

Fig. 1.2 The structure of a macromolecule corresponds to the internal structure of a metal or ceramic, if a primary structure is considered to be analogous to a molecular structure and a higher-order structure to a microstructure.

amorphous, it may be unreasonable to draw an analogy between them and metals or ceramics. However, if one thinks of a monomer as a unit of matter, one can regard a homopolymer as being roughly analogous to a pure metal and a copolymer to a solid solution.

These polymer structures are called *primary structures* in polymer science. In the first generation of polymers, such as nylon, invented in 1939, the main problems were designing and controlling the primary structures. However, certain polymers developed after 1970, such as Kevlar and supertough nylon, have controlled higher-order structures. Many of these polymers have molecular orientations that align as shown in Fig. 1.2(b1); others are alloys—combinations of two or more types of polymers—as shown in Fig. 1.2(b3). These examples indicate that higher-order structures of polymers are analogous to microstructures of metals or ceramics. Therefore, recently developed advanced polymers can be regarded as new materials that have been developed by *microstructure control* as the key technology.

Based on the previous discussion, the discipline of *materials science* would not exist today if not for the concept of microstructure. Therefore, *materials science* is distinguished from *matter science* (the branches of physical science devoted to the fundamental nature of matter) in this book; materials science is defined by the keyword of *microstructure* and matter science is not.

1.2 Matter Science: Its Short History (Ref 1)

1.2.1 Democritus's Atomic Theory

The starring actor in Act One of the history of matter science is the ancient Greek philosopher Democritus (Democritos), who studied and wrote on a wide range of disciplines, including physics, music, and ethics. Democritus is perhaps best known for his Theory of Atoms, which states that all matter is composed of *atoms*, which cannot be divided (*a* = not, *tom* = division).

His atomic theory was dismissed by Aristotle (Aristoteles) and his followers, who denied the concept of discontinuity. However, Democritus's theory later evolved to Sir Isaac Newton's corpuscular theory and A.L. Lavoisier's element theory. Some 2000 years after the Roman Era, with the intervening Middle Ages and Renaissance periods, these concepts have developed to the present theory of elementary particles, representing a splendid revival of Democritus's basic theory.

1.2.2 The Birth of Modern Chemistry

Although matter science stagnated in the Middle Ages, it developed rapidly in the latter half of the 18th century. The turning point was the discovery of oxygen by K.W. Scheele and J. Priestley in 1772. This discovery clarified the true character of oxidation and greatly accelerated the pace of discovery of new elements (see Fig. 1.3). This period also was the active age for the two scientists who founded modern chemistry, A. Lavoisier and J. Dalton (sometimes spelled Doulton).

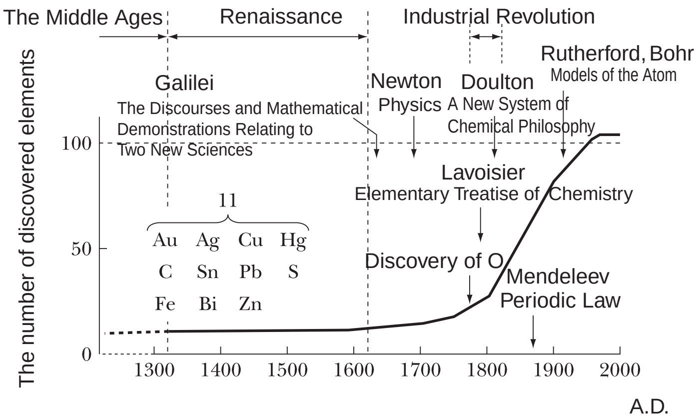


Fig. 1.3 The development of "matter science" (chemistry) versus that of physics

It is important to note that only 14 elements (the 11 in Fig. 1.3 plus As, Sb, and P) had been discovered by the time in the 17th century when Galileo (Galileo Galilei) and Newton founded physics. Matter science (chemistry), because of its complexity, was modernized at a pace far behind that of physics.

In 1789, the year of the French Revolution, Lavoisier, a hero of chemistry revolution, published his *Traité Élémentaire de Chimie* (*Elementary Treatise of Chemistry*) in which he presented the first table of the elements in history by grouping 33 elements (10 of which were not elements but compounds) into four groups. Dalton followed Lavoisier's unfinished work in his *New System of Chemical Philosophy* (1803), which presented atomic symbols and the atomic weights for 20 elements. D.I. Mendeleev, in 1869, completed the periodic law of the elements by consolidating the work of Lavoisier and Dalton.

After that, the existence of the electron and the atomic nucleus was confirmed by J.J. Thomson (1903) and E. Rutherford (1911). Act Two in the drama of matter science history reached its climax in 1913 when N.H.D. Bohr presented his Atom Model, which represents the atom as a small, positively charged nucleus orbited by electrons.

1.3 Establishment of Metallography

1.3.1 Discovery of Microstructure

A "microstructure world" exists between the "macroscopic world" of daily life and the "atomic and molecular world" of the fundamental elements of matter (Fig. 1.4). It was R. Hooke, famous for his law of elasticity, who first investigated this world of microstructure.

Hooke was an excellent experimental scientist of the same generation as Newton. He influenced scientists in many fields by publishing in

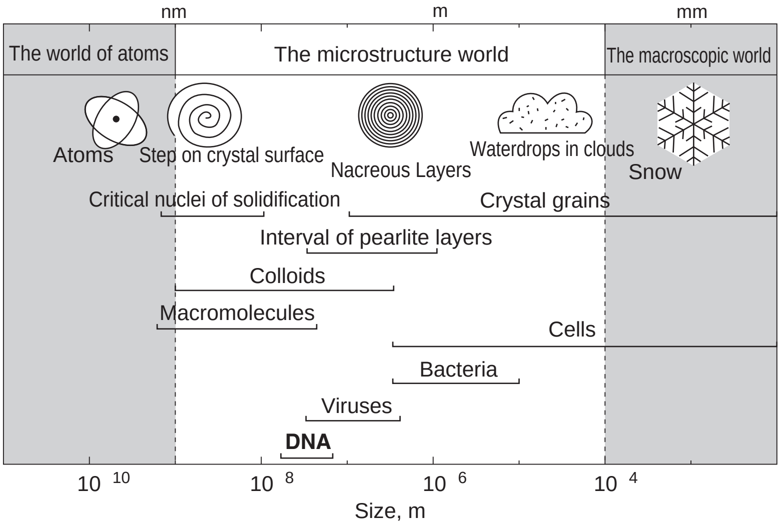
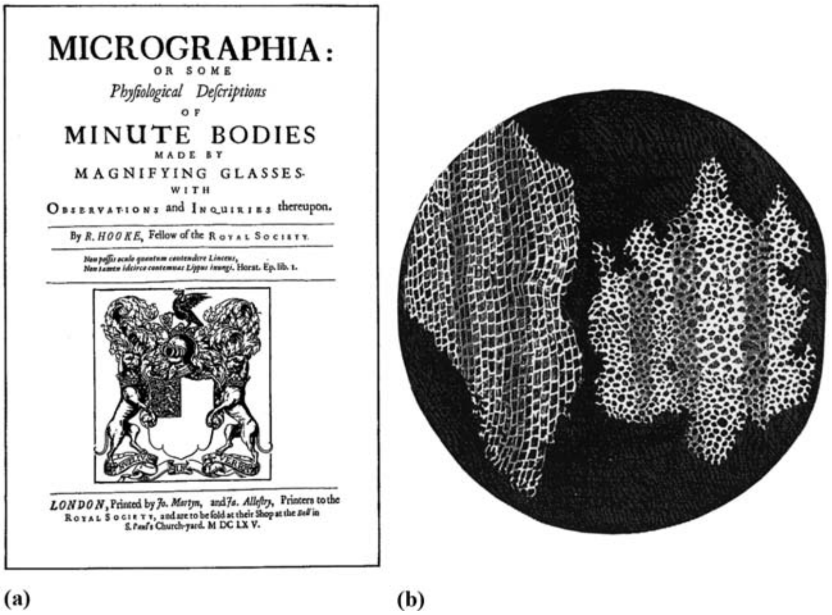


Fig. 1.4 The microstructure world. The words *micro* and *macro* come from the Greek words *mikros* and *makros*. Here, the boundary between both of them is set at the resolution of the naked eye (0.1 mm).


MICROGRAPHIA:
OR SOME
Phyſiological Deſcriptions
OF
MINUTE BODIES
MADE BY
MAGNIFYING GLASSES.
WITH
OBSERVATIONS and INQUIRIES thereupon.

By *R. HOOKE*, Fellow of the ROYAL SOCIETY.

Non poſſis oculo quantum contendere Linceus,
Non tamen idcirco contemnas Lippus inungi. Horat. Ep. lib. 1.

LONDON, Printed by *Jo. Martyn*, and *Ja. Alleſtry*, Printers to the
ROYAL SOCIETY, and are to be ſold at their Shop at the *Bell* in
S. *Paul's* Church-yard. M DC LX V.

Fig. 1.5 *Micrographia* by R. Hooke. (a) Cover. (b) A sketch of cork cells by Hooke

1665 his spectacular book *Micrographia*, which was full of sketches of microscopic objects (Fig. 1.5). In particular, his sketches of living cells represented monumental discoveries that later became the foundation of histology and bacteriology (Ref 2).

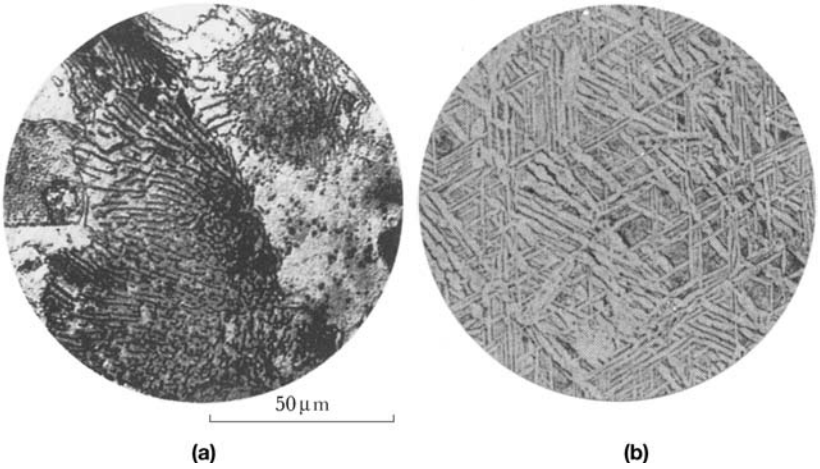


Fig. 1.6 Historically important microstructure and macrostructure. (a) The pearlite structure of carbon steel (microscope image of Sorby's sample owned by the University of Sheffield, 500×) (b) The Widmanstätten structure of iron-nickel meteoric iron (the section was polished and etched, and lithographically printed)

In 1863, 200 years after the publication of *Micrographia,* H.C. Sorby discovered that the microstructure world exists also in steel and that the strength of steel is remarkably affected by its microstructure (Fig. 1.6a). However, it was not easy for others to believe that a microstructure similar to that of living cells exists in a lump of iron appearing as flat and smooth as *Noppera-bō*, a Japanese mythological faceless creature. For this reason, it was not until 1885, 22 years after Sorby's discovery, that his micrographs were first printed in *Journal of the Iron and Steel Institute* (Ref 3–5).

As for the macroscopic structures of a metal, water patterns (ripple marks) in Japanese swords and Damascene swords had long been widely noted. Moreover, the macrostructure of the iron meteorite (Fig. 1.6b) that was presented in 1820 by A. von Widmanstätten, the superintendent at the Technical Museum, Vienna, is as beautiful as recent award-winning metallographic photographs. However, his contribution is just an episode in the history of understanding microstructure because it occurred before basic concepts of crystallography were established, such as Miller index (1839) and Bravais lattice (1848) (Ref 6).

On the other hand, Sorby, born and raised in the town of iron and steel, Sheffield, England, applied methods for observing the microstructure of a rock to steel. He succeeded in establishing the basic metallographic method that is used today, involving a series of operations: reveal microstructure by grinding and etching a sample cut on a plane and observe it using a reflecting microscope.

It is said, ''Science begins by observation.'' Sorby followed this path and thus became the father of metallography.

1.3.2 From Observation to Science

Hooke and Sorby opened the door to the ''microstructure world.'' The resolving power of today's electron microscopes has brought observers to the threshold of the ''atomic and molecular world,'' below the nanometer scale.

However, one cannot understand the essence of ''things'' only from accumulating the results of observation. A philosophy beyond observation, especially one based on thermodynamics, was needed so that metallography might be made a science instead of just a technique.

Thermodynamics, the branch of physics and of chemistry that studies the effects of changes in temperature, pressure, and volume on physical systems at the macroscopic scale, was developed during the Industrial Revolution, which started in the latter half of the 18th century. Its First Law, ''the law of conservation of energy,'' states that the change in the internal energy of a closed system is equal to the sum of the amount of heat energy supplied to the system and the work done on the system. Next, the concept of *entropy* (a measure of the energy in a system or process that is unavailable to do work) was established through an effort to improve the efficiency of engines. The Second Law of Thermodynamics posits that the total entropy of any isolated thermodynamic system tends to increase over time, approaching a maximum value. Thermodynamics as a way of thinking based on these two laws spread to various fields of science from the latter half of the 19th century to the beginning of the 20th century. Since that time it has led to the development of concepts of *chemical thermodynamics,* where the primary object is analyzing chemical reactions, and *statistical thermodynamics,* in which thermodynamic principles are joined with statistical mechanics (Fig. 1.7).

The pioneer of *thermodynamics of microstructure* was J.W. Gibbs of Yale University in the United States. He published a series of papers from 1873 to 1879 collectively titled *On the Equilibrium of Heterogeneous Substances*. In these papers Gibbs established or clarified basic concepts such as *phase*, *phase equilibrium*, and *chemical potential,* which are necessary to grasp the essence of microstructure, and defined his Phase Rule. In addition, he paid special attention to the concept of *interfaces,* describing accurate examinations of adsorption at an interface and internal pressure by interface tension (Ref 7).

These papers by Gibbs were full of very important ideas, but they were too difficult for scientists at the time to understand. However, they were spread in Europe through a German version by F.W. Ostwald (1891), or other versions, and have since developed into a vast system of study as shown in Table 1.1.

Because the main topics in Table 1.1 are explained in detail in the following chapters, the historical overview is discussed a little more here.

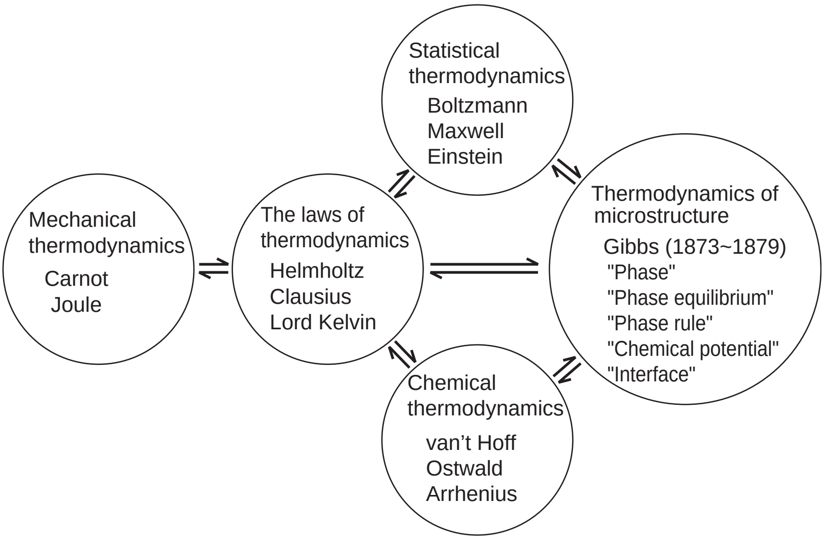


Fig. 1.7 The genealogy of thermodynamics and its development into the thermodynamics of microstructures

Table 1.1 Thermodynamics of microstructure chronology

Year (A.D.)	Researcher	Subject of study
1800	Gibbs	Advocate of thermodynamics of microstructures
	Austen	Phase diagram of Fe-C system
1900	Tammann	Textbook on physical metallurgy
1920	Volmer-Weber	Thermodynamics of nucleation
	Bragg-Williams-Gorsky	Ordering in solid solutions
	Johnson-Mehl-Avrami-Kolmogorov	Equation of transformation
1940	Zener-Smith	Pinning of grain boundaries
	Cottrell	Locking of dislocations
	Jackson	Roughness of solid/liquid interface
	Cahn-Hilliard-Hillert	Spinodal decomposition
1960	Lifshitz-Wagner	Ostwald ripening
	Kaufman-Hillert	Calculation of phase diagrams

1.4 Flowering of Materials Science

1.4.1 Progress of Steel Technology

The fundamentals of metallography and microstructure founded by Sorby and Gibbs brought a revolution to research and development of materials, and new materials were put to practical use one after another.

It was metals technology, especially that of steel, that reached maturity first. Various special steels, such as high-strength steels and stainless steels, were developed from the end of the 19th century to the beginning of the 20th century (Fig. 1.8). In Japan, Kotaro Honda and Hiroshi Takagi invented the Kichizaemon Sumitomo (KS) magnet steel in 1917 and thus left their immortal footprints on the history of magnetic materials.

Year (A.D).	Metals	Ceramics	Synthetic polymers
1800	Lavoisier-Doulton: establishment of modern chemistry		Dumas: methyl group Kekule: benzene hexagonal ring structure Establishment of organic chemistry
1850	Sorby: Gibbs: Establishment of metallography	Graham: advocate of colloid Sigmondy: ultramicroscope Establishment of colloid science	
1900	High-strength steels Duralmin 18-8 stainless steel KS magnetic steel	Zakariazen: glass structure	Staudinger: advocate of polymer science
	Grain-oriented electromagnetic steel	OP magnet	Nylon
1950	Silicon transistor Shape memory alloy Microalloyed steel	Transparent alumina Optical fiber High-strength zirconia Superconducting oxides	Glass fiber reinforced plastics Carbon fiber reinforced plastics Multiphase polymers

Fig. 1.8 History of development in new materials. OP, oxide powder

1.4.2 Progress in Synthetic Polymers and Ceramics

Steel is a foundation of contemporary civilization because it is the basis for much of its infrastructure, such as buildings, bridges, and vehicles. However, not all structural materials are steels. In particular, nylon, invented by W.H. Carothers in 1937, was the first synthetic polymer material in history; its development can be considered as the trumpet call signaling the dawn of a New Materials Age.

Polymer science is a rising field that was first advocated as a distinct discipline by H. Staudinger in Germany around 1920, but it did not really get established until after World War II, as indicated in the right side of Fig. 1.8. However, synthetic polymers quickly advanced to the status of being one three major industrial materials, along with metals and ceramics, within only a quarter of a century after the development of nylon.

Unlike synthetic polymers, ceramics have been used in conventional forms such as brick, cement, and pottery since ancient times. However, these materials also benefited from the establishment of microstructure science, and many fine ceramics with various advanced applications were developed starting in the 20th century. An early example is the oxide powder magnet announced by Yogoro Kato and Takeshi Takei in 1933, marking the beginning of ceramic magnet technology; ceramics are now the most widely used magnetic materials.

1.4.3 Establishment and Development of Materials Science

The rapid appearance of the aforementioned new materials challenged the scientific establishment to reconsider the way that materials were studied, and in response the discipline of Materials Science was born in the 1960s.

The most important aim of Materials Science is to formulate a unified system of science and technology by rearranging and combining, as it were, in a cross-disciplinary manner, the ‘‘vertically structured’’ knowledge and techniques that have been established separately for the study and development of metals, ceramics, and polymers.

In early Materials Science, the study of metals was relatively more advanced, but today both ceramic science and polymer science have caught up to metals science, and now all three major categories of materials contribute advances that enlighten the others. For example, ‘‘polymer alloy’’ is a new material that has been developed by applying traditional metallurgical alloying techniques to polymers. In another example, the exceptional strength of glass fiber reinforced plastics pointed out the importance of ‘‘structure designing,’’ and these concepts became the foundation for the development of high-strength dual-phase steel, which has high strength as well as excellent ductility.

In future materials development, it is increasingly important that we pay attention to the influence of a material on the global environment at each step of manufacturing as well as its properties and characteristics for its intended application (Ref 8).

It thus will become more important from now on to learn and apply the universality and sense of balance peculiar to Materials Science covering a broad range of view, especially thermodynamics, the subject of this book.

Appendix: The Glass Fiber Reinforced Plastic “Magic Wand”

New records in the pole vault were set one after another in the 1960s. The key factor was the appearance of a pole made of fiber reinforced plastics; at the time it was called a ‘‘magic wand’’ (Fig. 1.9a).

The mechanics of the pole vault are complicated, and assuming direct conversion from the kinetic energy ($mV_0^2/2$) to the potential energy (mgh), and a bar height (h) of 5.1 m at the highest point, one can go over

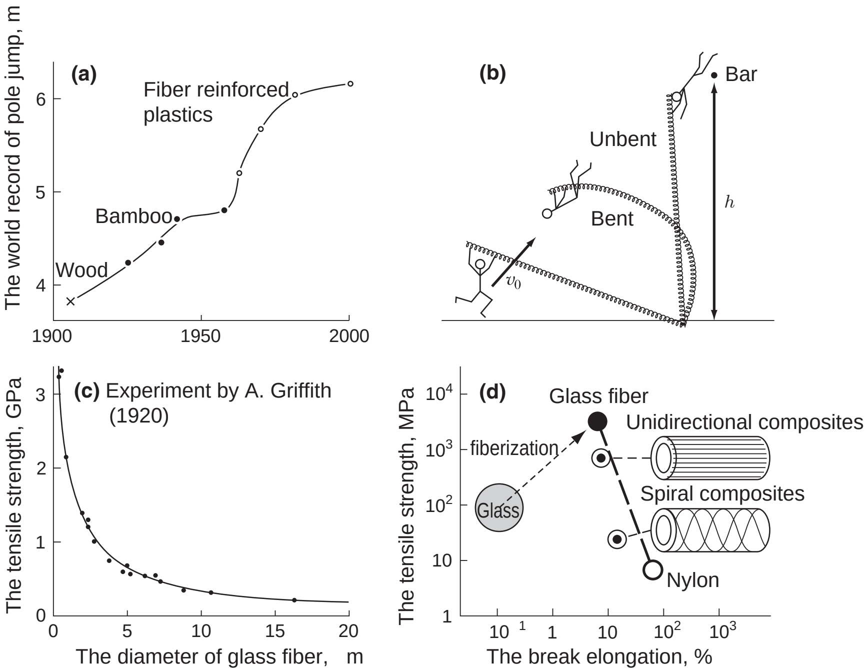


Fig. 1.9 The impact of materials technology on the sport of pole vaulting. (a) Relation between pole vault record and pole materials. (b) Mechanics of pole vault. (c) Strength of glass fiber. (d) Strength of glass fiber/nylon composite

when one approaches at the speed of 10 m/s, but this does not explain the record height of S. Bubka (6.14 m). Perhaps, the conclusive factor may be the force supplied by the moderate ‘‘bendability’’ and ‘‘restoring force’’ of the pole (Fig. 1.9b).

Glass will become remarkably stronger when it is drawn at a temperature over the softening point (approximately 1100 K) (Fig. 1.9c). Glass fiber reinforced plastic (GFRP) is a composite materials in which this fiber is arranged into plastic on the basis of structure design (Fig. 1.9d).

REFERENCES

1. M. Yuasa, *Pioneers in Materials Science,* Nippon Broadcast Association, 1976 (in Japanese)
2. NHK Nano-Space Project, *Inquiry into Ultramicroscopic World,* Nippon Broadcast Association, 1972 (in Japanese)
3. M. Nakazawa, *Fairy Tales on Iron (Pioneers in Metallurgy),* AGNE Publishing Co., 1975 (in Japanese)
4. C.S. Smith, *A History of Metallography,* University of Chicago Press, 1960
5. A.G. Quarrell, *Metallography—A Hundred Years after Sorby,* The Iron & Steel Institute, 1964

6. R.F. Mehl, On the Widmanstätten Structure, *The Sorby Centennial Symposium on the History of Metallurgy,* C.S. Smith, Ed., AIME, 1965, p 245–269
7. *Collected Works of J. W. Gibbs,* Longmans, Green & Co., 1928
8. K. Easterling, *Tomorrow's Materials,* 2nd ed., The Institute of Metals, 1990

EXERCISES FOR FURTHER STUDY

1.1 Investigate and describe the progress of microstructure observation from the magnifying glass to the electron microscope.

1.2 Various characteristics of a material are categorized roughly into ones that do not change so much, such as ''specific gravity,'' and others that change remarkably according to its microstructure, such as hardness. The former are called ''structure insensitive,'' and the latter ''structure sensitive.'' Choose three kinds of each characteristic and explain their relation to microstructure.

1.3 Describe the following inventions and discoveries and their impact on Materials Science from the standpoint of metallography: (1) Duralumin (1906), (2) thoriated tungsten (1917), (3) glass fiber reinforced plastic (circa 1940), (4) spheroidal graphite cast iron (1948), and (5) high-strength zirconia (1975).

Chapter 1: Introduction—An Overview of Microstructure in Materials

References

1. M. Yuasa, *Pioneers in Materials Science*, Nippon Broadcast Association, 1976 (in Japanese)

2. NHK Nano-Space Project, *Inquiry into Ultramicroscopic World*, Nippon Broadcast Association, 1972 (in Japanese)

3. M. Nakazawa, *Fairy Tales on Iron (Pioneers in Metallurgy)*, AGNE Publishing Co., 1975 (in Japanese)

4. C.S. Smith, *A History of Metallography*, University of Chicago Press, 1960

5. A.G. Quarrell, *Metallography—A Hundred Years after Sorby*, The Iron & Steel Institute, 1964

6. R.F. Mehl, On the Widmanstätten Structure, *The Sorby Centennial Symposium on the History of Metallurgy*, C.S. Smith, Ed., AIME, 1965, p 245–269

7. Collected Works of J. W. Gibbs, Longmans, Green & Co., 1928

8. K. Easterling, *Tomorrow's Materials*, 2nd ed., The Institute of Metals, 1990

Chapter 2: Free Energy of Pure Substances

References

1. “Standard for Use of the International System of Units (SI): The Modern Metric System,” IEEE/ASTM SI 10–1997, IEEE and ASTM International, 1997

2. *Corrosion:Fundamentals, Testing, and Protection*, Vol 13A, *ASM Handbook*, S. Cramer and B. Covino, Ed., ASM International, 2003

3. T. Usui, *Theory of Heat*, Tokyo University Press, 1969, (in Japanese)

4. R. Kubo, H. Ichimura, T. Usui, and N. Hashizume, *Theory of Heat and Statistical Mechanics*, Shoka Bo, 1961 (in Japanese)

5. R.A. Swalin, *Thermodynamics of Solids*, John Wiley & Sons, 1961.

6. C. Kittel, *Introduction to Solid State Physics*, 5th ed., John Wiley & Sons, 1976.

7. S. Chikazumi, *Physics of Magnetism*, John Wiley & Sons, 1964.

8. L. Kaufman, E.V. Clougherty, and R.J. Weiss, *Acta Metall.*, Vol 11, 1963, p 323 doi: 10.1016/0001-6160(63)90157-3

9. T. Nishizawa, Thermodynamics of Iron Alloys, *Bull. Jpn. Inst. Met.*, Vol 12, 1973, p 35, and p 333 (in Japanese)

10. Japanese Institute of Polymers, *Introduction to Polymer Science*, Tokyo Kagaku Dojin, 1978 (in Japanese)

11. M. Toda, H. Matsuda, Y. Hiwatashi, and M. Wadachi, *Structure and Properties of Liquid*, Iwanami Book Co., 1976 (in Japanese)

Chapter 3: Thermodynamics of Solutions

References

1. G.N. Lewis and M. Randall, revised by K.S. Pitzer and L. Brewer, *Thermodynamics*, McGraw-Hill, 1961

2. R. Kubo, H. Ichimura, T. Usui, and H. Hashizume, *Theory of Heat and Statistical Mechanics*, Shoka Bo, 1961 (in Japanese)

3. R.A. Swalin, *Thermodynamics of Solids*, John Wiley & Sons, 1962 doi: 10.1149/1.2425309

4. D.V. Ragone, *Thermodynamics of Materials*, Vol II, John Wiley & Sons, 1995

5. M. Hillert, *Phase Equilibria, Phase Diagrams and Phase Transformations. Their Thermodynamic Basis*, Cambridge University Press, 1998

6. A.K. Niessen *et al*., *Calphad*, Vol 7, 1983, p 51 doi: 10.1016/0364-5916(83)90030-5

7. M. Hillert and L.-I. Staffansson, *Acta Chem. Scand*., Vol 24, 1970, p 3618 doi: 10.3891/acta.chem.scand.24-3618

8. C. Wagner, *Thermodynamics of Alloys*, Addison-Wesley, 1952

9. S. Ban-ya, J.F. Elliott, and J. Chipman, *Metall. Trans*., Vol 1, 1970, p 1313 doi: 10.1007/BF02900248

10. C.H.P. Lupis and J.F. Elliott, *Trans. Met. Soc. AIME*, Vol 233, 1965, p 257

11. T. Nishizawa, K. Ishida, H. Ohtani, C. Kami, and M. Suwa, *Scand. J. Metall*., Vol 20, 1991, p 62

12. C.H.P. Lupis and J.F. Elliott, *Acta Metall*., Vol 14, 1966, p 1019 doi: 10.1016/0001-6160(66)90190-8

13. H. Tanaka, *Physics of Polymer*, Shoka Bo, 1994 (in Japanese)

14. H. Suzuki, *Introduction to Dislocation Theory*, AGNE, 1967, (in Japanese)

15. T. Aizawa, *Mater. Jpn*., Vol 36, 1997, p 930 (in Japanese) doi: 10.2320/materia.36.930

16. L. S. Darken and R. W. Gurry *Physical Chemistry of Metals*, McGraw-Hill, 1953, p 75–79

Chapter 4: Thermodynamics of Phase Diagrams

References

1. J.W. Gibbs, *Collected Works of J.W. Gibbs*, Vol I, *Thermodynamics*, Longmans, Green & Co., New York, 1928

2. L. Kaufman and H. Bernstein, *Computer Calculation of Phase Diagrams*, Academic Press, New York and London, 1970

3. N. Saunders and A.P. Miodownik, *CALPHAD (Calculation of Phase Diagrams)*, Pergamon, 1998, p 369–372

4. M. Hillert, *Phase Equilibria, Phase Diagrams and Phase Transformations. Their Thermodynamic Basis*, Cambridge University Press, 1998, p 377–378

5. J.L. Meijering, *Philips Res. Rep*., Vol, 5, 1950, p. 333; Vol 6, 1951, p 183

6. H.K. Hardy, *Acta Metall*., Vol 1, 1953, p 210 doi: 10.1016/0001-6160(53)90060-1

7. M. Hillert and L.I. Staffansson, *Acta Chem. Scand*., Vol 24, 1970, p 3618 doi: 10.3891/acta.chem.scand.24-3618

8. E. Rudy, *J. Less-Common Met*., Vol 33, 1973, p 43 doi: 10.1016/0022-5088(73)90056-8

9. H. Ohtani, K. Kojima, K. Ishida, and T. Nishizawa, *J. Alloys Compd*., Vol 182, 1992, p 103 doi: 10.1016/0925-8388(92)90579-X

10. A.J. Bradley, *J. Iron Steel Inst*., Vol 163, 1949, p 19; Vol 168, 1951, p 233; Vol 171, 1952, p 41

11. S.M. Hao, T. Takayama, K. Ishida, and T. Nishizawa, *Metall, Trans*., Vol 15A, 1984, p 1819 doi: 10.1007/BF02664895

12. H. Kaneko, M. Homma, K. Nakamura, M. Okada, and G. Thomas, *IEEE. Trans*. Vol 13, 1977, p 1325 doi: 10.1109/TMAG.1977.1059557

13. T. Nishizawa, Progress of CALPHAD, *Mater. Trans., JIM*, Vol 33, 1992 p 713 doi: 10.2320/matertrans1989.33.713

Chapter 5: Thermodynamics of Interfaces

References

1. R.A. Swalin, *Thermodynamics of Solids*, John Wiley and Sons, 1962 doi: 10.1149/1.2425309

2. L.E. Murr, *Interfacial Phenomena in Metals and Alloys*, Addison-Wesley, 1975

3. W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, *Introduction to Ceramics*, John Wiley and Sons, 1976

4. T. Sakurai and Y. Tamai, *Application of Interface Chemistry*, Asakura Book Co., 1967 (in Japanese)

5. R. Becker, *Ann. Phys.*, Vol 32, 1938, p 128 doi: 10.1017/S0009838800017900

6. J.D. Livingston and H.E. Cline, *Trans. Met. Soc. AIME*, Vol 245, 1969, p 351

7. N.B. Hannay, *Solid State Chemistry*, Prentice-Hall, 1967

8. D. McLean, *Grain Boundaries in Metals*, Oxford University Press, 1957

9. M. Hillert, *Lectures on the Theory of Phase Transformations*, H.I. Aaronson, Ed., AIME, 1975, p 36–44

10. M. Hillert, *Phase Equilibria, Phase Diagrams and Phase Transformations*, Cambridge University Press, 1998, p 392

11. M.P. Seah and E.D. Hondros, *Proc. R. Soc.*, Vol 335, 1973, p 191 doi: 10.1098/rspa.1973.0121

12. E.D. Hondros and M.P. Seah, *Int. Met. Rev.*, Vol 22, 1977, p 262 doi: 10.1179/imtr.1977.22.1.262

13. E.D. Hondros and M.P. Seah, *Metall. Trans.*, Vol 8A, 1977, p 1363 doi: 10.1007/BF02642850

14. T. Nishizawa, *ISIJ Int.*, Vol 40, 2000, p 1269 doi: 10.2355/isijinternational.40.1269

15. K.A. Jackson, *Liquid Metals and Solidification*, American Society For Metals, 1958; Kinetic Processes, Wiley-VCH, 2004, p 283–309

16. J.D. Hunt and K.A. Jackson, *Trans. Met. Soc. AIME*, Vol 236, 1966, p 843

17. A. Ookawa, *Crystal Growth*, Syokabo, 1977 (in Japanese)

18. B. Chalmers, *Principles of Solidification*, John Wiley and Sons, 1964

19. M. Hillert, *Acta Metall.*, Vol 13, 1965, p 227 doi: 10.1016/0001-6160(65)90200-2

20. C.S. Pande, *Acta Metall.*, Vol 35, 1987, p 2671 doi: 10.1016/0001-6160(87)90266-5

21. J.E. Burke and D. Turnbull, Recrystallization and Grain Growth, *Progress in Metal Physics 3*, B. Chalmers, Ed., Pergamon, 1952, p 220–292 doi: 10.1016/0502-8205(52)90009-9

22. P.G. Shewmon, *Diffusion in Solids*, McGraw Hill, 1963, p 171

23. K. Lücke and K. Detert, *Acta Metall.*, Vol 5, 1957, p 628 doi: 10.1016/0001-6160(57)90109-8

24. J.W. Cahn, *Acta Metall.*, Vol 10, 1962, p 789 doi: 10.1016/0001-6160(62)90092-5

25. M. Hillert, *Metall. Trans.*, Vol 6A, 1975, p 5 doi: 10.1007/BF02825676

26. T. Nishizawa, *Mater. Trans.*, Vol 42, 2001, p 2027 doi: 10.2320/matertrans.42.2027

27. Z. Jeffries and R.S. Archer, *The Science of Metals*, McGraw-Hill, 1924

28. L.S. Darken, R.P. Smith, and F.W. Filer, *Trans. AIME.*, Vol 191, 1951, p 1174 doi: 10.1007/BF03397430

29. C. Zener, quoted by C.S. Smith, *Trans. Met. Soc. AIME.*, Vol 175, 1948, p 15

30. F.J. Humphreys and M. Hatherly, *Recrystallization and Related Annealing Phenomena*, Elsevier Science, 1995, p 73–83 doi: 10.1016/B978-0-08-041884-1.50017-9

31. T. Nishizawa, I. Ohnuma, and K. Ishida, *Mater. Trans., JIM*, Vol 38, 1997, p 950 doi: 10.2320/matertrans1989.38.950

Chapter 6: Thermodynamics of Diffusion

References

1. M. Koiwa, Diffusion in Materials, Historical and Recent Developments, *Mater. Japan*, Vol 37, 1998, p 347 (in Japanese) doi: 10.2320/materia.37.347

2. A.D. Smigelskas and E.O. Kirkendall, *Trans. AIME*, Vol 171(1947), 130.

3. L.S. Darken, *Trans. AIME*, Vol 175, 1948, p 184

4. L.S. Darken, *Trans. AIME*, Vol 180, 1949, p 430

5. J. Groh and G.V. Hevesy, *Ann. Phys*., Vol 65, 1921, p 216 doi: 10.1002/andp.19213701103

6. P.G. Shewmon, *Diffusion in Solids*, McGraw-Hill, 1963

7. D.V. Ragone, *Thermodynamics of Materials*, John Wiley, 1995

8. W.D. Kingery, H.K. Bowen, and D.R. Uhlmann, *Introduction to Ceramics*, John Wiley, 1976, p 217–264

9. J. Woodford and Y.A. Chang, *Metall. Mater. Trans*., Vol 29A, 1998, p 2717 doi: 10.1007/s11661-998-0312-x

10. J.N. Hobstetter, Equilibrium, Diffusion and Imperfections in Semiconductors, *Prog. Metal Phys*., Vol 7, 1958, p 1–63 doi: 10.1016/0502-8205(58)90003-0

11. H. Gleiter and B. Chalmer, High-Angle Grain Boundaries, *Prog. Mater. Sci*., Vol 16, 1972, p 77–112

12. N.A. Gjostein, *Short Circuit Diffusion*, ASM Seminar on Diffusion, 1973, p 241–274

Chapter 7: Thermodynamics of Ordering

References

1. E.C. Bain, *Trans. AIME*, Vol 68, 1923, p 625

2. W.L. Bragg and E.J. Williams, *Proc. R. Soc.*, Vol A145, 1934, p 699

3. W.S. Gorsky, *Z. Phys.*, Vol 50, 1928, p 64 doi: 10.1515/crll.1928.159.50

4. H.A. Bethe, *Proc. R. Soc.*, Vol 150A, 1935, p 552 doi: 10.1098/rspa.1935.0122

5. R.H. Fowler and E.A. Guggenheim, *Proc. R. Soc.*, Vol A174, 1940, p 189

6. Y. Takagi, *Proc. Phys. Math. Soc. Japan*, Vol 23, 1941, p 44

7. R. Kikuchi, *Acta Metall.*, Vol 25, 1977, p 195. doi: 10.1016/0001-6160(77)90123-7

8. R. Kubo, H. Ichimura, T. Usui, and N. Hashizume, *Theory of Heat and Statistical Mechanics*, Shoka Bo, 1961, (in Japanese)

9. R.A. Swalin, *Thermodynamics of Solids*, John Wiley & Sons, 1962 doi: 10.1149/1.2425309

10. E. Fujita, *Metal Physics—Fundamentals of Materials Science*, AGNE Gijutu Center, 1996 (in Japanese)

11. R. Kikuchi and T. Mohri, *Cluster Variation Method*, Morikita Publishing, 1997 (in Japanese)

12. P.R. Swann, W.R. Duff, and R.M. Fisher, *Metall. Trans.*, Vol 3, 1972, p 409 doi: 10.1007/BF02642045

13. S.M. Allen and J.W. Cahn, *Acta Metall.*, Vol 23, 1975, p 1017 doi: 10.1016/0001-6160(75)90106-6

14. H. Kubo and C.M. Wayman, *Metall. Trans.*, Vol 10A, 1979, p 633 doi: 10.1007/BF02658327

15. L.D. Landau and E.M. Lifshitz, *Statistical Physics*, Addison-Wesley, 1958, p 439

16. M. Hillert, *Phase Equilibria, Phase Diagrams and Phase Transformations*, Cambridge University Press, 1998, p 385

17. H.K. Hardy, *Acta Metall.*, Vol 1, 1953, p 210 doi: 10.1016/0001-6160(53)90060-1

18. J.L. Meijering, *Philips Res. Rep.*, Vol 18, 1963, p 318 doi: 10.1016/0095-8522(63)90022-9

19. T. Nishizawa, M. Ko, and M. Hasebe, *Acta Metall*., Vol 27, 1979, p 817 doi: 10.1016/0001-6160(79)90116-0

20. H. Kaneko, M. Homma, and K. Nakamura, *AIP Conf. Proc*., Vol 5, 1971, p 1088

21. S.M. Hao, T. Takayama, K. Ishida, and T. Nishizawa, *Metall. Trans*. Vol 15A, 1984, p 1819 doi: 10.1007/BF02664895

Chapter 8: Thermodynamics of Nucleation

References

1. B. Vonnegut, *J. Colloid Sci.*, Vol 3, 1948, p 563 doi: 10.1016/S0095-8522(48)90049-X

2. D. Turnbull and R.E. Cech, *J. Appl. Phys.*, Vol 21, 1950, p 804 doi: 10.1063/1.1699763

3. J.H. Hollomon and D. Turnbull, Nucleation, *Prog. Met. Phys.* Vol 4, 1953, p 333 doi: 10.1016/0502-8205(53)90020-3

4. M. Volmer and A. Weber, *Z. Phys. Chem.*, Vol 119, 1926, p 277 doi: 10.1515/zpch-1926-11927

5. R. Becker and W. Döring, *Ann. Phys.*, Vol 24, 1935, p 719 doi: 10.1002/andp.19354160806

6. G. Borelius, *Ann. Phys.*, Vol 28, 1937, p 507 doi: 10.1002/andp.19374200603

7. J.L. Jorstad, *Trans. Met. Soc. AIME.*, Vol 242, 1968, p 1217

8. P.H. Shingu and J. Takamura, *Metall. Trans.*, Vol 1, 1970, p 2339 doi: 10.1007/BF02643459

9. H. Fujimura, S. Tsuge, Y. Komizo, and T. Nishizawa, *Tetsu-to-Hagane*, Vol 87, 2001, p 707 (in Japanese) doi: 10.2355/tetsutohagane1955.87.11_707

10. J.A. Marcantonio and L.F. Mondolfo, *Metall. Trans.*, Vol 2, 1971, p 465

11. H.J. Goldschmidt, *Interstitial Alloys*, Butterworths, 1967, p 273 doi: 10.1007/978-1-4899-5880-8

12. J.B. Clark, *Metals Handbook*, Vol 8, 8th ed., American Society For Metals., 1973, p 175

13. R.B. Nicholson and J. Nutting, *Acta Metall.*, Vol 9, 1961, p 332 doi: 10.1016/0001-6160(61)90227-9

14. F.R.N. Nabarro, *Proc. Roy. Soc.*, Vol 175, 1940, p 519 doi: 10.1098/rspa.1940.0072

15. I.S. Servi and D. Turnbull, *Acta Metall.*, Vol 14, 1966, p 161 doi: 10.1016/0001-6160(66)90297-5

16. N. Sano and Y. Maehara, *J. Jpn. Inst. Met.*, Vol 60, 1996, p 261 (in Japanese) doi: 10.2320/jinstmet1952.60.3_261

17. S. Kōda, O. Kōono, M. Nemoto, T. Takeyama, and H. Kimura, *Precipitation in Alloys*, Maruzen, 1972, (in Japanese)

18. W. De Sorbo, H.N. Treaftis, and D. Turnbull, *Acta Metall.*, Vol 6, 1958, p 401 doi: 10.1016/0001-6160(58)90019-1

19. A. Guinier, *Compt. Rend.*, Vol 206, 1938, p 1641; *Nature*, Vol 142, 1938, p 569 doi: 10.1038/142569b0

20. G.D. Preston, *Proc. Ry. Soc.*, Vol A167, 1938, p 534; *Nature*, Vol 142, 1938, p 570 doi: 10.1038/142570a0

21. V. Gerold, *Z. Metallkd.*, Vol 54, 1963, p 370 doi: 10.1515/ijmr-1963-540608

22. H.Y. Hunsicker and H.C. Stumpf, History of Precipitation Hardening, *The Sorby Centennial Simposium on the History of Metallurgy*, C.S. Smith, Ed., AIME, 1965, p 293

23. T. Konno, K. Hiraga, and M. Kawasaki, HAADF-STEM Obervation of GP zones in Aged Al-Cu Alloys, *Mater. Japan*, Vol 42, 2003, p 861 doi: 10.2320/materia.42.861

Chapter 9: Thermodynamics of Microstructure Change

References

1. J.W. Christian, *Transformations in Metals and Alloys*, Pergamon Press, 1965, p 9

2. W.A. Johnson and R.F. Mehl, *Trans. Met. Soc. AIME*, Vol 135, 1939, p 416

3. M. Avrami, *J. Chem. Phys.*, Vol 7, 1939, p 1103 doi: 10.1063/1.1750380

4. A.N. Kolmogorov, *Izv. Akad. Nauk, USSR*, Vol 1, 1937, p 355

5. H.I. Aaronson, C. Laird, and K.R. Kinsman, *Phase Transformations*, American Society for Metals, 1970, p 313

6. M. Enomoto, *Transformations in Metals*, Uchida Rokakuho Publishing, 2000, (in Japanese)

7. Y. Saito, *An Introduction to the Kinetics of Diffusion Controlled Microstructural Evolutions in Materials*, Corona Publishing, 2000, (in Japanese)

8. L.S. Darken and R.W. Gurry, *Physical Chemistry of Metals*, McGraw-Hill, 1953, p 397

9. P.G. Shewmon, *Diffusion in Solids*, McGraw-Hill, 1963, p 171

10. C. Wells, W. Batz and R.F. Mehl, *Trans. AIME*, Vol 188, 1950, p 553 doi: 10.1007/BF03399032

11. G.A. Chadwick, *Prog. Mater. Sci.*, Vol 12, 1964, p 97 doi: 10.1017/S0032247400054358

12. M.C. Flemings, *Solidification Processing*, McGraw-Hill, 1974, p 94

13. C. Zener, *Trans. AIME*, Vol 167, 1946, p 550

14. D. Turnbull, *Acta Metall.*, Vol 3, 1955, p 55 doi: 10.1016/0001-6160(55)90012-2

15. J.W. Cahn, *Acta Metall.*, Vol 7, 1959, p 18 doi: 10.1016/0001-6160(59)90164-6

16. V.F. Zackay and H.I. Aaronson, *Decomposition of Austenite by Diffusional Processes*, Interscience Publishers, 1962

17. D. Brown and N. Ridley, *J. Iron Steel Inst.*, Vol 204, 1966, p 811

18. J.S. Kirkaldy, *Met. Trans.*, Vol 4, 1973, p 2327 doi: 10.1007/BF02669371

19. F. Togashi and T. Nishizawa, *J. Japan Inst. Metals*, Vol 40, 1976, p 691, (in Japanese) doi: 10.2320/jinstmet1952.40.7_691

20. F.J. Humphreys and M. Hatherly, *Recrystallization and Related Annealing Phenomena*, Pergamon, 1995, p 136 doi: 10.1016/B978-0-08-041884-1.50017-9

21. T. Saito, T. Sakuma, and T. Nishizawa, *Trans. JIM*, Vol 21, 1980, p 471, 483 doi: 10.2320/matertrans1960.21.483