UNDERSTANDING MATERIALS SCIENCE

History ▪ Properties ▪ Applications

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Springer

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Preface

It is a challenging endeavor to trace the properties and the development of materials in the light of the history of civilization. Materials such as metals, alloys, ceramics, glass, fibers, and so on have been used by mankind for millennia. Actually, materials have shaped entire civilizations. They have been considered of such importance that historians and other scholars have named certain ancient periods after the material which was predominantly utilized at that respective time. Examples are the Stone Age, the Bronze Age, and the Iron Age. As time progressed the materials became increasingly sophisticated. Their properties were successively altered by man to suit ever-changing needs. We cannot but regard with utmost respect the accomplishments of men and women who lived millennia ago and who were capable of smelting, shaping, and improving the properties of materials.

Typical courses on world history expose students mainly to the description of major wars, the time span important rulers have reigned, and to the formation, expansion and downfall of world empires. Very little is generally said about the people who lived and toiled in ancient times and about the evolution of civilizations. This book traces the utilization, properties, and production techniques of materials from the Stone Age via the Bronze Age and the Iron Age up to modern times. It explains the physical properties of common materials as well as those of "exotic materials" such as superalloys, high-tech ceramics, optical materials, electronic materials, and plastics. Likewise, natural and artificial fibers and the technique of porcelain- and glass-making are covered. Moreover, this book provides a thorough introduction into the science and engineering of materials, covering all essential features that one would expect to find in a horizontally integrated introductory text for materials science. Specifically, the book presents the mechanical, electrical, magnetic, optical, and thermal properties of all materials including textiles, fibers, paper, cement, and wood in a balanced and easily understandable way. This book is not an encyclopedia of materials science. Indeed, it is limited in its depth so that the content can be conveniently taught in a one-semester (15-week), three-credit-hour course. Nevertheless, the topics are considered to be essential for introducing engineers and other interested readers to the fascinating field of materials science.

Plenty of applied problems are given at the end of the technical chapters. The solutions for them are listed in the Appendix. The presentation follows an unusual sequence, starting with a description of the properties of the first materials utilized by man, such as stone, fiber, and copper. Subsequently, the differences between these materials are explained by considering their atomistic structure, the binding forces between the atoms, and their crystallography. A description of the Bronze Age is followed by the treatment of alloys and various strengthening mechanisms which are achieved when multiple constituents are blended to compounds. The properties of iron and steel are explained only after an extensive history of iron and steel making has been presented. In Part II, the electronic properties of materials are covered from a historical, as well as from a scientific, point of view. Eventually, in Part III the historic development and the properties of ceramics, glass, fibers and plastics as we understand them today are presented. The book concludes with a chapter on economics, world resources, recycling practices, and ecology of materials utilization. Finally, an outlook speculating on what materials might be utilized 50 years from now is given. Color reproductions of relevant art work and artifacts are included in two inserts to show the reader how materials science is interwoven with the development of civilization.

This book is mainly written for engineering, physics, and materials science students who seek an easily understandable and enjoyable introduction to the properties of materials and the laws of physics and chemistry which govern them. These students (and their professors) will find the mixture of history, societal issues, and science quite appealing for a better understanding of the context in which materials were developed. I hope, however, that this book also finds its way into the hands of the general readership which is interested in the history of mankind and civilization as it relates to the use and development of materials. I trust that these readers will not stop at the end of the historical chapters, but instead will continue in their reading. They will discover that the technical sections are equally fascinating since they provide an understanding of the present-day appliances and technical devices which they use on a daily basis. In other words, I hope that a sizeable readership also comes from the humanities. Last, but not least, future archaeo-metallurgists should find the presentation quite appealing and stimulating.

A book of this broad spectrum needs, understandably, the advice of many specialists who are knowledgeable in their respective fields. It is my sincere desire to thank all individuals who in one way or another advised me after I wrote the first draft of the manuscript. One individual above all stands out particularly: Dr. Volkmar Gerold, Professor Emeritus of the University of Stuttgart and the Max-Planck-Institut for Materials Research who read the manuscript more than once and saw to it that each definition and each fact can stand up to the most rigid scrutiny. My sincere thanks go to him for the countless hours he spent on this project.

Other colleagues (most of them from the University of Florida) have read and advised me on specific chapters. Among them, Dr. R.T. DeHoff (diffusion and general metallurgy), Dr. A. Brennan (polymers), and Dr. E.D. Verink (corrosion) are particularly thanked. Further, Drs. C. Batich and E. Douglas (polymers), Drs. D. Clark, J. Mecholsky, and D. Whitney (ceramics), Dr. C. Beatty (recycling), Dr. J.D. Livingston (MIT; magnetism), Dr. C. Pastore (Philadelphia College of Textiles and Science; fibers), Mr. E. Cohen (Orlando, FL) and Mr. R.G. Barlowe (U.S. Department of Agriculture, World Agricultural Outlook Board) need to be gratefully mentioned. Ms. Tita Ramirez cheerfully typed the manuscript with great skill and diligence. Finally, Dr. M. Ludwig carried on my research work at those times when my mind was completely absorbed by the present writings. To all of them my heartfelt thanks.

Rolf E. Hummel
Gainesville, FL
April 1998

Contents

PART I

MECHANICAL PROPERTIES OF MATERIALS

1

The First Materials (Stone Age and Copper–Stone Age)

Materials have accompanied mankind virtually from the very beginning of his existence. Among the first materials utilized by man were certainly stone and wood, but bone, fibers, feathers, shells, animal skin, and clay also served specific purposes.

Materials were predominantly used for tools, weapons, utensils, shelter, and for self-expression, that is, for creating decorations or jewelry. The increased usage and development of ever more sophisticated materials were paralleled by a rise of the consciousness of mankind. In other words, it seems to be that advanced civilizations generally invented and used more elaborate materials. This observation is probably still true in present days.

Materials have been considered of such importance that historians and other scholars have named certain ancient periods after the material which was predominantly utilized at that respective time. Examples are the *Stone Age*, the *Copper–Stone Age (Chalcolithic*[1] *Period)*, the *Bronze Age*, and the *Iron Age*. The Stone Age, which is defined to have begun about 2.5 million years ago, is divided into the *Paleolithic* (Old Stone Age), the *Mesolithic* (Middle Stone Age), and the *Neolithic* (New Stone Age) phases. We will consider on the following pages mostly the Neolithic and Chalcolithic periods. Surprisingly, these classifications do not include a *Ceramics Age*, even though pottery played an important role during extended time periods (see Chapter 15).

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[1]*Chalcos* (Greek) = copper; *lithos* (Greek) = stone.

The names of some metals have entered certain linguistic usages. For example, the Greeks distinguished the *Golden Age* (during which supposedly peace and happiness prevailed) from the *Silver Age*. Rather than being descriptive of the materials that were used, these distinctions had more metaphorical meanings. Specifically, gold has always been held in high esteem in the eyes of mankind. Medals for outstanding performances (sport events, etc.) are conferred in gold, silver, or bronze. Specific wedding anniversaries are classified using gold, silver, and iron.

Until very recently, the mastery of materials has been achieved mainly by empirical means or, at its best, by a form of alchemy. Only in the nineteenth and twentieth centuries did systematic research lead to an interdisciplinary field of study that was eventually named *materials science*. This will be explained and demonstrated in detail in later chapters.

Materials often have to be cut, shaped, or smoothed before they reach their final form and designation. For this, a tool that is harder than the work piece has to be set in action. As an example, flint stone having a sharp edge was used by early man for cutting and shaping other materials such as wood.

The simplest and most common method of making stone tools from bulk rocks was by *percussion flaking*. Specifically, a lump stone was struck with another stone to detach small pieces from it. If these flakes happened to have sharp edges, they could be used as cutting tools. In early times, the tools were hand-held. Later (probably 5,000–10,000 years ago), stone flakes were attached to wooden handles using fibers or vegetable resin. This provided for better leverage, thereby amplifying their impact. Other flakes may have been used as spear or arrow tips, etc. (see Plate 1.1).

Fishing hooks were made from shell and bone. Ground mineral pigments were used for body painting. Grass fibers (e.g., flax, hemp, etc.) or animal hair (wool) served as clothing and for holding loose objects together. Jade, greenstone, and amber were utilized for adornments. This list could be continued.

Stones, particularly flint and obsidian (a dark grey natural glass that precipitated from volcanic emissions, see Plate 1.2) were available to Neolithic man in sufficient quantities at certain locations. Because of their abundance and their sharp edges, stones filled the needs as tools and weapons. Thus, it is not immediately evident why mankind gradually switched from a stone-using society to the metals age.

This transition, incidentally, did not occur at the same time in all places of the world. The introduction of metals stretched over nearly 5,000 years, if it occurred at all, and seems to have begun

FIGURE 1.1. Copper pendant found in a cave in northeast Iraq; about 9500 B.C. The shape was obtained by hammering native copper or by carving copper ore. (Reprinted by permission from C.S. Smith, *Metallurgy as a Human Experience* (1977), ASM International, Materials Park, OH, Figure 2.)

independently at various locations. For example, metals were used quite early in Anatolia, the bridge between Asia and Europe (part of today's Turkey),[1] where a highly developed civilization existed which cultivated seed-bearing grasses (wheat and barley) and domesticated such animals as cattle, sheep, and goats. The transition from a nomadic to a settled society left time for activities other than concerns for everyday gathering of food. Thus, man's interest in his environment, for example, in native copper, gold, silver, mercury, or lead, is understandable.

Neolithic man must have found out that metals in their *native* state (that is, not combined with other elements, as in ores) can be deformed and hardened by hammering or can be softened by heating. Pieces of native metals were probably quite valuable because they were rare. Still, these pure metals were generally too soft to replace, to a large extent, tools and weapons made of stone. Thus, pure metals, particularly *copper, silver,* and *gold,* were mostly used for ceremonial purposes and to create ornaments or decorations. As an example, one of the very earliest copper artifacts, a 2.3-cm long, oval-shaped pendant is shown in Figure 1.1. It was found in a cave in northeast Iraq (Shanidar). It is believed that it has been created around 9500 B.C. by hammering native copper or possibly by carving copper ore. Utensils made of metal must have lent some prestige to their owner. Copper, in particular, played an outstanding role because of its appearance and its relative abundance (especially after man learned how to smelt it). In short, the stone and copper ages coexisted for a long

[1]See the map on the rear endpaper for locations cited in the following discussion.

time. This led to the above-mentioned name, Chalcolithic, or Copper–Stone Age.

Eventually, native copper and other metals must have been nearly exhausted. Thus, Neolithic man turned his attention to new sources for metals, namely, those that were locked up in minerals. A widely used copper ore is malachite (Plate 1.3). It is plentiful in certain regions of the earth such as in Anatolia, Cyprus, or on the Sinai peninsula. Now, the smelting of copper from copper ore, that is, the separation of copper from oxygen, sulphur, and carbon, was (and is), by no means, a trivial task. It requires intense heat, that is, temperatures above the melting point of pure copper (1084°C) and a "reducing atmosphere"; in other words, an environment that is devoid of oxygen and rich in carbon monoxide. The latter is obtained by burning wood or charcoal. When all conditions are just right, the oxygen is removed from the copper ore and combines with carbon monoxide to yield gaseous carbon dioxide, which is allowed to escape. Finally, a *fluxing agent*, for example, iron ore, assists in the reduction process. It also aids eventually in the separation of the molten copper from the slag once the melt has cooled down. Specifically, iron ore combines with the unwanted sand particles that just happen to be contained in the ore.

The immense heat was accomplished by burning charcoal combined with blowing air into the furnace either by mechanically activated bellows or through blow tubes (called tuyères) (Figure 1.2), or by placing the furnace near the top of a mountain where the updraft winds were utilized. It is still a mystery today how Neolithic man could have found this chain of procedures without a certain degree of intuition or possibly the help of initiates.

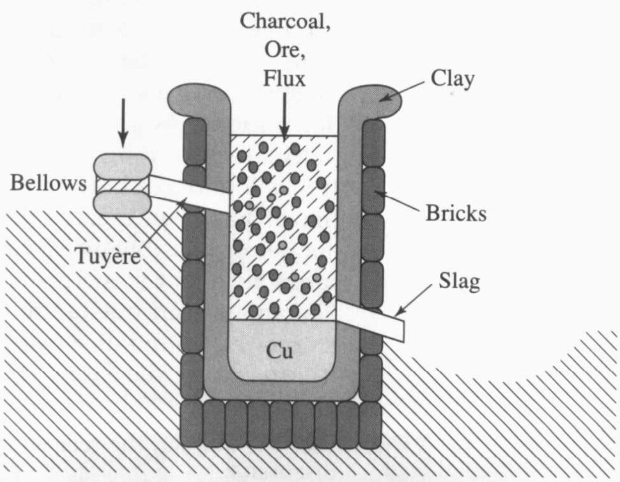

FIGURE 1.2. Schematic representation of an ancient copper smelting furnace which was charged with a mixture of charcoal, copper ore, and flux (e.g., iron ore). The oxygen was provided by forcing air into the furnace by means of foot-operated bellows.

Archaeo-metallurgists have recently ruled out the hypothesis that copper could have been accidentally formed in campfires whose enclosures may have consisted of copper-ore–containing rocks. The temperatures in campfires (600–700°C) are known to be too low for smelting copper and the reducing atmosphere does not persist for a long enough time. (However, lead, which has a lower melting temperature, can be smelted this way from its ore.)

It is believed today that the "technology" of copper smelting was probably borrowed from the art of making pottery, which was developed nine or ten thousand years ago or perhaps even earlier at certain locations. Indeed, the oldest known artifact made of baked clay is a fertility figurine called the "Venus of Vestonice," which was found in the Czech Republic and supposedly dates back to about 23,000 B.C. (see Figure 15.1). In general, however, copper smelting and pottery seem to appear at comparable times in history. Specifically, Neolithic man had observed that mud bricks harden when dried in the sun and soften when again exposed to rain. A deliberate attempt to accelerate the drying process by exposing the mud bricks to the heat of a fire probably led to the observation that an irreversible hardening process had occurred. A chemical transformation near 500°C causes a permanent consistency of clay which makes it water-resistant. It can be reasonably assumed that this observation eventually led to the systematic development of the art of pottery and the design of kilns instead of drying clay over or under an open fire. Neolithic man must have observed that stacking pots on top of wood fuel and covering this pile with fragments of pottery and earth would increase the temperature. Eventually, kilns with permanent walls were developed, parts of which still exist today, dating back to the beginning of the sixth millennium B.C. We shall return to this subject in Chapter 15.

Neolithic people have decorated some pottery utilizing probably the same ground-up metal ores (mixed with a lead oxide binding agent) that were used customarily for tribal body painting. Various metal oxides produce different colors. Pigments of copper oxide, for example, yield a blue color, chromium oxide gives green, antimony salts yield yellow, and iron yields pink hues after a second firing of these "glazes." Could it have been that the overfiring of glazed pots accidentally produced small droplets of metals, that is, caused some smelting of metal ores in the glazed areas?

Another question remains to be answered. Was copper smelting conceived of independently in different parts of the world, or was this technology transferred from neighboring regions through trading contacts? Possibly both happened. Among the first civilizations to utilize copper smelting were probably the inhabitants of Anatolia (Catal Hüyük) and of the Sinai peninsula (Timna Valley), both blessed with rich and abundant copper ores on or near the surface. On the other hand, copper (and gold) objects have been found in graves at Varna on the Black Sea dating back to about 4300 B.C. (Plate 1.4).

Naturally, raw copper needed to be transported to other places where goods were produced from it. For standardization, copper ingots were cast in a peculiar form that resembled the shape of an ox hide, as shown in Figure 1.3. A vivid depiction of ancient copper smelting and casting has been found on a mural in the tomb of an Egyptian nobleman; see Figure 1.4.

Seemingly independent from this development, Europeans had turned, out of necessity, to underground copper mining even before 4000 B.C. (for example, at Rudna Glava in Yugoslavia). One mine in Bulgaria was found to have shafts about 10 meters deep. The copper mines on the Balkans are the earliest so far discovered in the world. Other indigenous copper workings were discovered in southern Spain (Iberia) and northern Italy. The dislodging of rocks in mines was accomplished by burning wood at the end of a tunnel and then quenching the hot rock with water. This caused the rock to crack so that small pieces could be loosened with a pick. Underground mining must have been a large-scale operation that involved workers who supplied the fuel, others who were involved in transportation, and naturally the actual miners.

Subsurface ores are often more complex in composition than those found on the face of the earth. In particular, they contain sulfur that needs to be removed before smelting. For this, a separate heating process, which we call today "roasting," needed to be applied.

Among the earliest metalworkers in Europe were people in whose graves characteristic bell-shaped clay cups have been

FIGURE 1.3. Copper ingots were traded in the Mediterranean region in an *ox-hide* shape having a length of about 30 cm. Specimens have been found in shipwrecks off the south coast of Turkey and in palace storerooms in Crete. (See also Figure 4.1.) Incidentally, raw gold was traded in the form of large rings.