Dedicated to the memory of Nancy Ferguson Frye (1943–1975)

Copyright © 1981 by Hutchinson Ross Publishing Company
Library of Congress Catalog Number: 81-982
ISBN: 0-87933-184-4

All rights reserved. No part of this book may be reproduced or transmitted in any form or by any means—graphic, electronic, or mechanical, including photocopying, recording, taping, or information storage and retrieval systems—without written permission of the publisher.

85 84 83 82 81 5 4 3 2 1
Manufactured in the United States of America.

Library of Congress Cataloging in Publication Data

Main entry under title:
The Encyclopedia of mineralogy.
(Encyclopedia of earth sciences; v. 4B)
Includes bibliographies and indexes.
I. Mineralogy—Dictionaries. I. Frye,
Keith, 1935- . II. Series.
QE355.E49 549'.03'21 81-982
ISBN 0-87933-184-4 AACR2

Distributed worldwide by Academic Press,
a subsidiary of Harcourt Brace Jovanovich,
Publishers.
METALLIC MINERALS


META-AUTUNITE GROUP—See AUTUNITE GROUP

METALLIC MINERALS

Of the three classes of economic minerals (metallic minerals, mineral fuels, and industrial minerals), metallic minerals are those that may be used as a source of one or more metals. There are over 300 metallic minerals, the majority being sulfides and sulfosalts (60%) followed by oxides (25%) and native elements (10%).

If we ignore the early use of native elements (q.v.), the first use of metallic minerals as ores was about 4000 BC when reduction of “oxidized zone” copper ores, probably mainly malachite, to metal was first discovered. Later, the join
METALLURGY

Metallurgy as a field of engineering is concerned with the art and science of producing and adapting metals to satisfy human wants. The science of metallurgy is involved with the study of metals, their physical and chemical properties. It is usually divided into two related areas, chemical and physical metallurgy.

Chemical metallurgy concerns itself with the extraction of metals from their ores, the refining of metals, and the thermodynamics that control these processes. Metals are mainly obtained from ores, naturally occurring aggregates of metallic oxide or sulfide minerals, which are present in the earth's crust. The chemical metallurgist develops processes for the making of a concentrate containing the ore minerals (ore dressing) of interest and the reduction of these ores to the metallic state. Three types of reduction processes are available:

1. Pyrometallurgy is the chemical reduction of ores by smelting at high temperatures (1000–2000°C). This process is by far the most important commercially. The reactions are carried out in furnaces with refractory linings of alumina-siliceous or siliceous material. Many of the most important commercial metals and alloys, iron and steel, nickel, copper, and zinc, are produced by this process.

2. Hydrometallurgy is the leaching of ores and concentrates with aqueous solutions to dissolve and recover primarily the precious metals.

3. Electrometallurgy is the use of electric current for chemical reduction. This process is employed to refine such metals as copper, zinc, and lead from impure metals. Aluminum is obtained electrolytically from molten salts of the metals.

The most important pyrometallurgical processes are those used for producing pig iron and steel. Iron ore is first reduced with coke in a blast furnace. Limestone is added to react with the siliceous impurities in the ore and coke ash to form a fusible slag. Such a slag is mainly lime, alumina, and silica with smaller amounts of magnesia and iron oxide. After the pig iron is produced, it is refined to make steel in an open hearth or basic oxygen furnace. The

References


Cross-references: Electron Probe Microanalysis; Mineral and Ore Deposits; Native Elements and Alloys; Optical Mineralogy; Ore Microscopy; see also mineral glossary.
METALLURGY


The basic oxygen process, which employs an oxygen lance positioned directly in the molten metal, is a recent development. This process is now used to produce most of the steel in the United States.

Metallurgists are just beginning to understand the thermodynamics that underlie these various chemical reduction processes. Particular attention is being paid to the thermodynamics and kinetics of slag-metal interactions. Computers are now used to model the processes and to calculate the thermodynamics and heat balances that control the processes.

Physical metallurgy concerns itself with the structure and properties of metals. This area of metallurgy probably had its beginning in 1808 when Alois de Widmanstätten polished the surface of an iron meteorite and discovered the pattern that bears his name. The Widmanstätten pattern of the Carlton meteorite is shown in Fig. 1. The pattern is made up of kamacite (α iron) in a parent matrix of taenite (γ iron). In and around 1890, mainly as a result of the work of Sorby in England, metallography, the observation of structural details of metals, began to be used to relate metallic structure to properties. Physical metallurgy has expanded greatly since the late 1800s and now consists of four main areas: (1) atomic theory and physical properties, (2) phase relationships, (3) mechanical properties, and (4) engineering alloys—materials.

Atomic Theory and Physical Properties

Several of the major topics of concern in physical metallurgy are bonding, atomic structure, and imperfections. Metallic bonding involves the attractive forces between the free outer-shell electrons and the positive-charged ions. The free-electron cloud is largely responsible for the high electrical and thermal conductivity of metals; and the free electrons absorb light energy, making them opaque to transmitted light. Also, because of the metallic bonding, the crystal structure of metals are mainly cubic.

Among the physical properties of interest to the metallurgist are the electrical, thermal, thermoelectric, magnetic, and optical properties. With respect to magnetic properties, iron, cobalt, nickel, and some specialty alloys exhibit ferromagnetism, an electrostatic interaction between adjacent atoms that aligns the resultant spins of the atoms. Only magnetite (Fe₃O₄) and pyrrhote (Fe₁₋ₓS) are common magnetic minerals. Most metals are paramagnetic: most nonmetals are diamagnetic, i.e., very weakly repelled by a magnetic field (see Magnetic Minerals).

Phase Relationships

The area of phase relationships in metallurgy concerns itself with phase diagrams, solidification, and solid state reactions. In most cases, the metallurgist is able to use binary (two-component) phase diagrams effectively, while the geologist is concerned with more complicated systems (see Vol. IVA: Phase Equilibria). Various phase relationships of interest to metallurgists are the binary solid-solution series, intermediate phases, and, in solidification, the eutectic and peritectic reactions.

In solidification processes, complete equilibrium can only be approached between solid and liquid under slow rates of cooling. Therefore, most alloys experience nonequilibrium solidification, where concentration gradients are developed in the solid phase. These gradients greatly influence the properties of the final alloy. The process of zone melting, however, has been used to purify metals (see Crystal Growth).

In solid-state transformations, the eutectoid reaction and precipitation from solid solution are very important. Solid-state reactions occur much more slowly than in solidification processes due mainly to low diffusion rates. They are subject to greater supercooling and rarely have the compositions given by the phase diagram. The crystal structure of the new phase has a definite orientation relationship to the crystal structure of the phase from which it formed, as in formation of the Widmanstätten pattern (Fig. 1).

The most serious problem in the commercial application of equilibrium diagrams is the fact that examination of the diagram is often not practical.
that equilibrium is not often attained. An example of this can be found in the commercially important Fe base alloys (steels) which contain 0.1 to 1.5 wt % carbon. At a carbon content of 0.8%, a eutectoid reaction (austenite-pearlite) occurs. If the cooling rate of the steel is slow, a plateletlike mixture of austenite and pearlite is formed. If the cooling rate is increased, however, bainite or martensite or mixtures of these constituents may also be produced.

Mechanical Properties

The high strength and ductility of metals and alloys makes them ideally suited for structural applications. Mechanical properties of materials are often subdivided into the elastic and plastic ranges. In the elastic range, no permanent effect is produced by stresses, and in the plastic range, large deformations of metal parts occur. Since many finished products are to be used in the elastic range, a high yield strength and high Young's modulus is desired. Alloying and temperature can, however, affect these properties significantly.

Metal plasticity is particularly important in the forming operations that are carried out on all wrought metals. Rolling or forging of steel at high temperatures must be done at a rate determined by the deformation characteristics of the individual alloy. Cold forming operations, so important in the mass production of many metal parts, are even more restricted by plastic properties. Of particular concern to the metallurgist is the process of fracture, final failure. This physical phenomenon is often studied by various types of tests (tensile, impact, torsion, fatigue) to understand the mechanism and mode of failure.

Engineering Alloys and Materials

The engineering metallurgist focuses attention upon the relation between microstructures and properties, using the phase relationships (phase diagrams) as a guide in designing better alloys. However, much of the knowledge in this field still is on an empirical basis. Table 1 lists properties of many alloys in copper, aluminum, and steel alloys (Ruoff, 1973). The variety of mechanical properties obtained and the possible applications of these alloys is almost endless. In recent years, however, the metallurgist who must make selections of materials has become much more materials oriented and has extended his knowledge of materials selection to all types of materials; e.g., plastics, semiconductors, and ceramics.

Two areas of research in metallurgy have important bearing on the geochemical problems associated with the structure and composition of the earth and other planetary bodies. One of these is the effect of pressure on the phase relations of iron; the other is the effect of time, temperature, and pressure on the development of the structure of metal phases in meteorites and lunar samples. Pressure has a large and significant effect on the transition temperature for phase equilibria and phase transformations in metals (Kaufman, 1963). According to the Clapeyron-Clausius equation:

\[
\frac{dP}{dT} \Delta H = T_m \Delta L \frac{\Delta T}{T_m^2}
\]

<table>
<thead>
<tr>
<th>Table 1. Mechanical Properties of Various Metal Alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Material</strong></td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>OFHC 99.95% annealed copper</td>
</tr>
<tr>
<td>OFHC 99.95% cold-drawn copper</td>
</tr>
<tr>
<td>99.45% annealed aluminum</td>
</tr>
<tr>
<td>99.45% cold-drawn aluminum</td>
</tr>
<tr>
<td>2024 (3.8–4.9% Cu, 0.3–0.9% Mn, 1.2–1.8% Mg) heat treated aluminum alloy</td>
</tr>
<tr>
<td>1020 steel (0.2% C)</td>
</tr>
<tr>
<td>1095 steel (hardened) (0.95% C)</td>
</tr>
<tr>
<td>4340 annealed alloy steel</td>
</tr>
<tr>
<td>4340 fully hardened alloy steel</td>
</tr>
<tr>
<td>Maraging (300) steel</td>
</tr>
</tbody>
</table>

Adapted from Ruoff, 1973.

a OFHC means oxygen-free high-conductivity.

b 4340 steels are 1.65–2.0% Ni, 0.4–0.9% Cr, 0.2–0.3% Mo, 0.4% C, remainder Fe.
METALLURGY

for the transition α→γ, solid to liquid, where 

$$T_A$$ is the melting temperature and 

$$P$$ is the pressure. 

$$L$$ is the latent heat of phase change, and 

$$\Delta V$$ is the difference in volume of the phases.

$$\left(\frac{dT}{dP}\right)_{\alpha\rightarrow\gamma} = T_A \left(\frac{\Delta V}{L}\right)_{\alpha\rightarrow\gamma}$$

for the transition α→γ where 

$$T_A$$ is the transition temperature for the polymorphic reaction 

α→γ. The effect of increased pressure in pure iron, for example, is to raise the transition temperature for α(bcc)→Liq and to decrease the transition temperature for the reaction α(bcc)→γ(fcc).

The classical interpretation of the composition of the earth's core is that it is similar to the composition of iron meteorites, i.e., iron-nickel alloys with about 10 wt% nickel. Several significant effects have been reported from studies of Fe-Ni alloys at high pressures. At 25°C and 130 kilobars, the transition α→γ occurs, forming a new compact hexagonal phase (Mao et al., 1967). However, the addition of Ni to iron in the γ phase makes the material more compressible than pure iron at high pressures (McQueen and Marsh, 1966). Extrapolations to pressures and temperatures at the earth's core, assuming that the structure of the solid core is γ phase, indicate that the iron-nickel alloy would be about 10% heavier than pure iron.

However, density data determined by geophysical measurements indicates that the density of the earth's core is 10-15% less than the density of pure iron at comparable pressures, 14 to 3.4 megabars, and temperatures, greater than 4000°K. It has been suggested (Birch, 1952) that, if iron is the major component of the core, elements of lower density would be alloyed with iron. A number of light elements that would lower the density of iron or iron-nickel alloys in the core has been proposed, but the two most seriously considered at the present time are silicon and sulfur. A core of Fe-Ni-S has also been proposed for the moon (Brett, 1973). Since all the conclusions about the composition of the earth's core are derived from extrapolations from laboratory experiments, the nature of the earth's core is still very much open to question.

The Widmanstätten pattern in iron meteorites (Fig. 1) was developed as the meteorites cooled through the temperature range 700-300°C while the meteorites were yet a part of a planetary or asteroidal body. The α (kamacite) phase nucleated from the parent γ (taenite) phase, forming a Widmanstätten pattern, and grew by solid-state diffusion. Electron microprobe analysis of these phases has shown that they are not at equilibrium. However the Ni gradients measured by the microprobe in kamacite and taenite can be used to determine the rate at which equilibrium is approached.

It has been possible to simulate the growth process for the Widmanstätten pattern by a metallurgical analysis (Wood, 1964; Goldstein and Olgivie, 1965), since the factors that control the growth process—the iron-nickel phase diagram and interdiffusion coefficients—are well known. These simulation studies have allowed determination of the cooling rates of the parent bodies of the iron meteorites. The cooling-rate values determined to date (Goldstein and Short, 1967) range between 0.5 and 500°C/m yr. They indicate that iron meteorites have formed in more than one parent body and have parent-body sizes in the asteroidal size range (20-350 km) not in the planetary range. The internal pressures of these parent bodies are less than a few kilobars. Recent evidence has also suggested that not all of the iron meteorites form in the core of their respective parent bodies. It is apparent, however, that the effects of elements such as P, C, and S must be considered when discussing the development of the Widmanstätten structure in iron meteorites (Goldstein and Axon, 1973).

Until recently, the only source of extraterrestrial metal has been in the meteorites that have landed upon earth. It is now possible to study metal that has been returned from the moon. Two populations of lunar metal have been recognized (Frondel, 1975): (1) metal of meteoritic origin that has been subject to greater or lesser degrees of metamorphic change in the lunar crust or on the moon's surface, and (2) metal that is the result of igneous fractional crystallization of lunar rock, vapor condensation, or shock reduction of iron-bearing lunar minerals. The history and origin of lunar metal is presently a subject of intense research.

JOSEPH I. GOLDSTEIN

References


METAMICT STATE

Broegger (1893) recognized that some minerals that show crystal form are, nevertheless, structurally amorphous but have attained this state in a different manner than glasses or rigid gels. He wrote: “For this third class of amorphous substances there is proposed the name metamict (from μεταμικτός, mix otherwise, that is by a molecular rearrangement to another structure than the original crystalline) amorphous substance. The reason for the amorphous rearrangement of the molecules might perhaps be sought in the lesser stability which so complicated a crystal molecule as that of these minerals must have in the presence of outside influences.”

Properties

Many of the features of metamict minerals had been recognized earlier; some were not recognized till a later date. The more significant features are:

1. Optically isotropic—Many metamict substances are heterogeneous, being partly isotropic and partly anisotropic.

2. Pyrographic, i.e., readily becoming incandescent on heating—In this regard there is great variation, no glowing being observable in some cases. Even strongly pyrographic minerals such as gadolinite can be annealed below the temperature of glowing with complete loss of the pyrographic quality.

3. Lacking in cleavage, fracture conchoidal—Some are also particularly brittle.

4. Density increased by heating—The change may be slight.

5. Crystalline structure reconstituted by heating—Reconstruction may be a complex process. Even if a single phase results it is usually polycrystalline.

6. Resistance to attack by acids is increased by heating—This is just the opposite of the effect produced by heating in most substances.

7. Contain uranium (U) or thorium (Th)—The content may be low, e.g., 0.41% ThO₂ in gadolinite from Ytterby, Sweden. The presence of rare earths and related elements has been emphasized by some observers.

8. Some known in both the crystalline and metamict states—In these cases little chemical difference can be found. There is evidence of hydration attending isomorphization but no direct or general correlation has been established.

9. X-ray amorphous—Vegard (1916) first reported the absence of X-ray diffraction by thorite. This has since been noted for many other metamict minerals and is now regarded as the typical test. Some traces of X-ray diffraction may be observed though the minerals have become optically quite isotropic.

Causes

It is now generally agreed that α-particle bombardment is the cause of isomorphization. In fact, some physicists have used the expression metamict in writing of radiation damage. Many minerals are known in the metamict state, some only in this state; but many natural compounds of radioactive elements are never found in this state. Goldschmidt (1924) enumerated three conditions required for metamictization:

A. The original structure must be only weakly ionic and possibly susceptible to hydrolysis.

B. The structure must contain one or more kinds of ions that are readily susceptible to changes in the state of ionization.

C. In many cases, it may additionally be necessary that the crystal is subjected to relatively strong radiation, either from radioactive material within the crystal or from outside sources.

Mechanism

Metamictization is doubtless similar to the more rapid processes of radiation damage in technological materials, which have recently received much attention. Only a small part of the energy of the α particles is effective in producing structural damage. Directly or indirectly, through recoil atoms, α particles displace structural units, giving rise to vacancies and interstitial atoms. Some of the energy is converted to heat, which may locally bring about melting. Whether minerals become metamict may depend on the extent to which they recover from the damage by natural annealing.

Occurrence of Metamict Minerals

Scores of different mineral species are known in the metamict state. Many are characteristic...