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镁合金冶金基本原理

Fundamentals of magnesium alloy metallurgy

Edited by Mihriban O. Pekguleryuz, Karl U. Kainer
and A. Arslan Kaya

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影印版说明

本书介绍了镁合金冶金的基本理论和技术，主要包括：镁的物理冶金、镁合金的热力学性能、镁合金的沉淀析出过程、镁的合金化及镁合金设计、镁合金成形、镁合金腐蚀及表面处理等，重点介绍了镁合金及镁基复合材料在航空、汽车、医疗器械等领域的应用。

本书对镁合金熔炼及成形加工技术的研究和生产具有参考价值，适合冶金、材料加工等行业的工程技术人员使用，也可供高等院校相关专业的师生参考。

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1
Primary production of magnesium

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Abstract: This chapter reviews the production technology for a variety of magnesium processes developed over the past 150 years on a commercial scale. It discusses why processes vary considerably in the case of magnesium, unlike the case of aluminum production.

Key words: magnesium, light-weight structural metal, molten chloride electrolytic process, thermal reduction, Pidgeon process, electro-thermal.

1.1 Introduction

Magnesium ion is the most abundant structural metal ion in the ocean; it is the fifth most abundant element in the hydrosphere (3.1×10^{15} tons). In the earth's crust (lithosphere) magnesium is considered to be the eighth most abundant element. If we consider the topmost 3.8 km, magnesium is the third most abundant 'structural metallic element'. It should be noted that the average depth of the ocean is 3.8 km – this is the hydrosphere, where magnesium is the only extractable structural metal. This makes magnesium a unique structural element, which can be extracted from either the hydrosphere or the lithosphere. Aluminum is sparse in the ocean, and is extracted from the lithosphere only.

As we all know, manmade materials are made by processes using the raw materials available, or which can be acquired at a low cost while converting them to a value-added material. Irrespective of the source of the raw material, additional energy matter is required to effect the conversion of the mineral into metal. The nature and cost of the energy and energy materials have been important factors in the choice of the process development of magnesium.

Since magnesium is available from the lithosphere and the hydrosphere, various routes are available for extraction into metal. This chapter is written so as to take us through the history of commercial processes in the nineteenth and twentieth centuries, before discussing the chemistry of process evolution, steps involved in production methods, and major equipment needed for different processes. Following this, future possibilities are discussed.

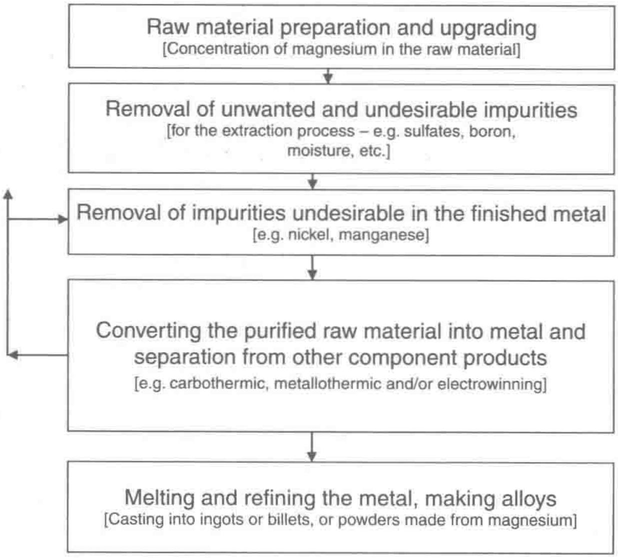
It took over 18 years of laboratory and pilot research, with personal attention given by Herbert H. Dow between 1896 and 1915, before a commercial line for producing magnesium came on line. It took another 16 years before reducing the cost of a pound of magnesium from 5 dollars to about 30 cents by the early 1930s. The process was further refined over the years in reducing operating costs (Campbell and Hatton, 1951). Dow Magnesium had a production of over 100 000 tons per year in its peak years during its 80 plus years of operation before being shut down in 1997.

The same period saw the development of magnesium for structural applications, both in the USA as well as in Germany. Dow Chemical is credited with introducing Dow-Metal pistons for the automotive sector in the 1920s, while the Germans developed a magnesium alloy engine for Volkswagen in the 1930s, helped by I.G. Farbenindustrie's magnesium process. Herbert H. Dow also pioneered the introduction of magnesium into the construction of aircraft in the early 1920s (Campbell and Hatton, 1951), even though this pioneering effort was not able to compete with aluminum – which is 1.5 times heavier than magnesium. We still continue to revisit this subject time and again, even to the present day, in educating the public about the benefits of magnesium alloys as a structural metal and the fact that magnesium can be safely used (Gwynne, 2010). With the advent of higher strength magnesium alloys, magnesium composites can compete with fiber reinforced composites in alternative energy generation such as wind power, etc.

Unlike for other metals, the processes used in the production of magnesium have gone through several historic changes – almost following the changes in the economic dominance history on a global scale – whether it be the world wars, or the cold war through the 1980s, or the emergence of the global economy in the 1990s, and through the recent commodity rise and fall during 2006–9. In 1935, John A. Gann, Chief Metallurgist of The Dow Chemical Co., noted the following '... our light metals occur only in the form of compounds so stable that their discovery, isolation, commercial production, and use were forced to await some of the modern advances in chemistry and engineering. Under such conditions, the evolution of a new industry is often a romance in which scientific and industrial difficulties and near failures add to the thrill of success' (Gann, 1935). The truth of this statement has been proved time and again in the production processes, even in recent times, and in the further development and uses of magnesium.

All magnesium metal production processes go through the following unit process steps (see Fig. 1.1):

i. Raw material upgrading
ii. Removal of unwanted and undesirable impurities



1.1 General flow sheet for magnesium production.

iii. Removal of impurities undesirable in the finished metal
iv. Converting the purified raw material into metal and separation from other component products – along with processing and or reuse of other raw material components
v. Melting, refining and casting metal and/or alloys
vi. Granular magnesium and alloys.

1.2 Raw materials and production methods

Most of the metallic elements are usually extracted or reduced from their respective oxides, or oxide compounds. The lithospheric compounds from which magnesium is extracted are: dolomite ($CaCO_3{\cdot}MgCO_3$), magnesite ($MgCO_3$), periclase (magnesium oxide) (MgO), hydro-magnesite ($3MgCO_3{\cdot}Mg(OH)_2{\cdot}3H_2O$), brucite ($MgO{\cdot}H_2O$), and silicates of magnesium (olivine$(Mg,Fe)_2SiO_4$, serpentine $3MgO{\cdot}2SiO_2{\cdot}2H_2O$ with partial iron substitution of magnesium, fosterite, *biotite micas*, etc.). The lithospheric minerals magnesium sulfate (epsomite- $MgSO_4{\cdot}7H_2O$), kieserite ($MgSO_4{\cdot}H_2O$), langbeinite ($K_2SO_4{\cdot}2MgSO_4$), and kainite ($KCl{\cdot}MgSO_4{\cdot}3H_2O$), carnallite ($KCl{\cdot}MgCl_2{\cdot}6H_2O$) are of hydrospheric origin found in evaporites.

The hydrosphere – oceans, and terminal lakes – has magnesium as the second most abundant metallic cation in the salinity. Sodium, present in a larger quantity, usually provides the ionic balance for the chloride ion in saline waters; sulfate is needed to provide ionic balance of magnesium along with chloride ions. Magnesium minerals found from the evaporites in the chloride form include carnallite ($KCl{\cdot}MgCl_2{\cdot}6H_2O$) and bischofite ($MgCl_2{\cdot}6H_2O$). Many of these were identified initially in Stassfurt, Germany in the mid-nineteenth century. Most of the process variations have been caused by the choice of raw material, whether it is oxide or a chloride type material, as we will see in the forthcoming discussions.

1.2.1 Nineteenth century magnesium production processes

In 1808, Humphry Davy took moistened magnesium sulfate and electrolyzed it onto a mercury cathode. He also converted red hot magnesium oxide with potassium vapor, collecting the magnesium into mercury. Both processes produced magnesium amalgam, from which he made the metal by distilling out the mercury. In 1828, Bussy reduced magnesium chloride with potassium metal in a glass tube; when the potassium chloride was washed out, small globules of magnesium were present.

Faraday in 1833 electrolyzed impure magnesium chloride in a molten state to get magnesium metal; but it took two more decades before Robert Bunsen made a commercial quantity in a small laboratory cell using molten anhydrous magnesium chloride. He noted the need to dehydrate the magnesium chloride for improving the electrolysis by avoiding sludge formation. Bunsen demonstrated in 1852 that it is easier to dehydrate magnesium chloride in a potassium chloride bath – this later led to the use of naturally occurring carnallite as a source for making magnesium. Commercial production of magnesium on a larger scale was initiated in 1886 – about the same time as the beginnings of the Hall–Heroult cell for aluminum.

Since oxide magnesium ores, such as MgO, are found in high grade (90% plus purity), attempts were made to use this as feed material using a molten fluoride melt – similar to the Hall–Heroult cell during the late nineteenth century. But the high melting point of magnesium fluoride above 950°C, along with the low solubility of magnesium oxide even in these fluorides, and the high vapor pressures of magnesium at these temperatures, made the growth of these processes uneconomical and difficult.

Molten dehydrated carnallite ($KCl{\cdot}MgCl_2$) was electrolyzed to magnesium metal in 1886 by the Aluminium und Magnesium Fabrik, Germany. This was further developed by Chemische Fabrik Griesheim-Elektron starting in 1896 – this became I.G. Farbenindustrie in the twentieth century. Molten carnallite electrolysis still continues in the twenty-first century, with various improvements made in the twentieth century.

1.2.2 Commercial magnesium production processes of the twentieth century

Several in-depth articles, as well as books, are available on the commercial production technologies of magnesium. These references are highlighted, avoiding duplication of detail on the processes currently used.

In 1938, Haughton and Prytherch noted that the extraction of magnesium followed three processes – electrolysis of fused chlorides, electrolysis of the oxide in solution of molten fluorides, and direct reduction of the oxide by carbon in an arc furnace with a hydrogen atmosphere followed by re-distillation in inert atmosphere. World War II brought the silico-thermic reduction of oxides to the fore. At this time, the production of magnesium was one third that of aluminum worldwide (Haughton and Prytherch, 1938).

Unlike aluminum, the demand for magnesium took a precipitous drop following World War II, causing the variation of production technology processes. Carbo-thermic and fluoride-melt electrolytic processes exited commercial production. Silico-thermic processes took a backseat, until the mid 1990s, to the electrolytic conversion of magnesium chlorides.

China entered the global economy in the early 1990s, interested in developing uses for its *apparently* very low-cost ferro-silicon. China, a non-market economy, thus revived magnesium oxide conversion by the silico-thermal method into a dominant process of the first decade of the twenty-first century.

Some of the early history of processes in the first half of the twentieth century is given in articles or chapters in books (Emeley, 1967; Ball, 1956; Beck, 1939; Schambra, 1945). At the time of writing (2010), the production of magnesium has narrowed to two main processes – one from lithospheric magnesium mineral dolomite by the thermal process, and the other from hydrospheric magnesium chloride. It is now felt that the abundance of magnesium resources, the evolution of non-fossil alternative energy, the realization of a global market economy (where costs of raw materials are a significant issue), along with the development of new uses for magnesium and its alloys, can alter this dominance by two main processes during the next 70 years.

Evans gives a concise summary of the evolution of commercial processes in the light metals aluminum, magnesium and lithium over the last five decades (Evans, 2007). Habashi presented a history of magnesium in a 2006 symposium (Magnesium technology in the Global Age) held in Montreal (Habashi, 2006). Production technologies of magnesium, a chapter by, Eli Aghion and Gilad Golub, discusses present day electrolytic as well as thermal reduction processes (Aghion and Golub, 2006). An in-depth history of magnesium by Robert E. Brown discusses the production of magnesium