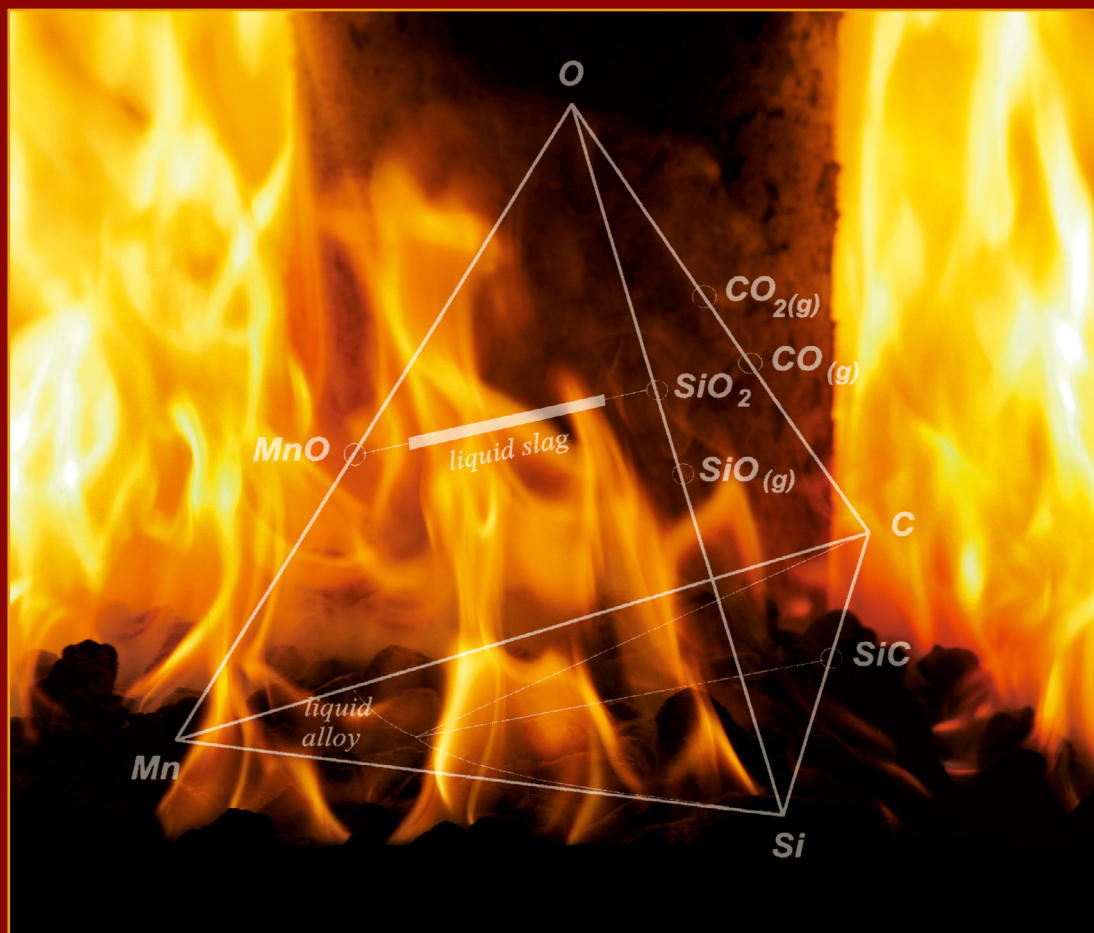


Production of Manganese Ferroalloys



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Adapted for ebook by John Grieg, Bergen

ISBN: 978-82-450-4614-4 (ebook)
1. edition, 1. version 2023
Ebook is based on 1st edition of paper book: ISBN: 978-82-519-2191-6
Language consultant: Catriona Turner
Prepress and layout: Type-it AS

ACKNOWLEDGEMENTS

The Norwegian Ferroalloy Producers Research Association (FFF) for support
The Norwegian University of Science and Technology (NTNU) for support
SINTEF; The Foundation for Scientific and Industrial Research at NTNU for support
Financial support from the NTNU/SINTEF CarboMat project sponsored by The Research Council of Norway and FFF
Kai Tang, (PhD) SINTEF, for thermodynamic calculations and preparation of equilibrium and phase diagrams
Norbert Volkmann, Professor, TU-Bergakademie Freiberg for advice on Section 3.3 Carbon materials
Eivind Hoel, (PhD), for main contributions to Section 4.4 Post tap-hole processing
Leif Hunsbedt, M.Sc, Tinfos Manganese for supplying various pictures
Rio Doce Manganese Norway for supplying front cover photo
M.Sc. students, PhD students and post doctoral researchers at NTNU, and researchers at SINTEF, who have carried out research work within the scope of this book

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www.fagbokforlaget.no

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Preface

The development of manganese alloys manufacturing processes to the present standard of efficiency has largely been brought about by trial and error and by experience gained under production conditions. The chemistry of the processes has often been limited to a list of chemical reactions which are believed to have taken place. However progress in our knowledge of thermodynamics and physico-chemical factors, which determine the rate and extent of the various reactions, has developed rapidly during the past twenty-five years or so, and it is now possible to define precisely equilibrium conditions and the factors affecting the kinetics of many of these reactions.

The aim of this book is to present principles and current knowledge of the processes in the production of high carbon ferromanganese, silicomanganese and low carbon manganese alloys. The book is intended for professionals working in production, plant design or development as well as for researchers in industry, universities and research institutes. The book can be used as a textbook for courses on extractive and process metallurgy, and for company in-house courses.

We have chosen a level of presentation that we think is suitable for most readers with sufficient knowledge of chemistry and thermodynamics. The thermodynamics of the slag and metal systems are extensively covered. Computational modelling based on assessed thermochemical databases has made it possible to calculate and present a large number of phase diagrams and equilibrium diagrams for easy understanding and analyses of the complex heterogeneous equilibria in the manganese ferroalloy metallurgy. Also experimental data are presented to verify the computed diagrams. Kai Tang (SINTEF) has been of invaluable help for carrying out all thermodynamic calculations and for preparing the majority of the diagrams.

The core of the process is the furnace where the manganese alloys are produced by carbothermic reduction of the manganese oxide ores. High carbon ferromanganese is mainly produced in electric submerged arc furnaces and to a lesser degree in blast furnaces. Silicomanganese is only produced in submerged arc furnaces. This book

covers mainly the submerged arc processes, although the chemistry is the same in both processes. Electrical relations are briefly discussed. Supply of raw materials, especially manganese ores and coke, is extremely important for the manganese industry. The book aims to give the reader appropriate knowledge to select the best of available raw materials.

Environmental issues, including greenhouse gas and climate change, are a growing concern for the ferroalloys industry, which cannot adapt by complete change of process. They will always need to use carbon and to emit CO₂. The book gives the reader a brief description of how to solve pollutions problems and the latest guidelines for greenhouse gas inventories.

It is impossible to cover extensively every aspect of manganese alloy production within this book. However, a comprehensive list of references is included where we have provided sources which we consider will give readers in-depth knowledge of specific topics.

We hope that this book will serve as a basis for present knowledge and for further research and development.

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Chapter 1

History of manganese

Manganese is a relatively common element in the earth's crust. The average concentration reaches nearly 0.1%, and it is the twelfth most abundant element and fourth most abundant of the metals in commercial use. Pure manganese is a metallic element with specific gravity in the range 7.21–7.44 kg/dm³ depending on its allotropic form. The melting point is 1244°C and the boiling point 2060°C. It can have the valences 1, 2, 3, 4, 6, and 7. The pure metal is greyish-white, resembling iron, but it is harder and very brittle. Manganese (Mn) and iron (Fe) are close neighbours in the periodic system, with element numbers 25 and 26 and atomic weights 55 and 56 respectively.

Manganese occurs in nature in the form of minerals. These are mainly oxides, carbonates and silicates. Mn-rich minerals are the main compounds of manganese ores. Paintings pigmented with manganese dioxide can be traced back 17000 years. Later, in ancient Greece, the presence of manganese in steel gave the Spartans superior steel weapons. The Egyptians and Romans used manganese compounds in glass making, either to remove colour from glass or to add colour to it. The very useful laboratory reagent potassium permanganate was first produced in the 17th century by the German chemist Johann Glauber. By the mid-18th century, manganese dioxide was in use in the manufacture of chlorine. In 1774, the Swedish chemist Carl Wilhelm Scheele was the first to recognize that manganese is a separate chemical element, and in the same year his colleague Johan Gottlieb Gahn isolated an impure sample of the element by reduction of manganese dioxide (pyrolusite) with charcoal. At the beginning of the 19th century, scientists began to explore the use of manganese in steelmaking, with patents being granted for its use. In 1816, it was found that adding manganese to iron made it harder, without making it more brittle.

A blast furnace was first used for commercial production of ferromanganese. The produced alloy was actually pig iron with 10–20% manganese, in German called *spiegeleisen*. The major breakthrough in the use of manganese occurred in 1860. At that time, Sir Henry Bessemer was trying to develop the steelmaking process which was subsequently to bear his name. However, he experienced difficulty with an excess of

residual oxygen and sulphur in the steel. The problems were overcome through the beneficial effect of manganese, disclosed in a patent granted to Robert Mushet in 1856. Mushet suggested adding *spiegeleisen* after the blow to introduce both manganese and carbon and to remove oxygen. This procedure made the Bessemer process possible, and thus opened the way for the modern steel industry. Ten years later, in 1866, William Siemens patented the use of ferromanganese in steelmaking to control the levels of phosphorus and sulphur. The commercial production of ferromanganese with *c.* 65 % manganese content started in France in 1875.

From *c.* 1890 high carbon ferromanganese was also produced by carbothermic reduction in electric furnaces, and silicothermic and aluminothermic reduction processes were developed to produce refined manganese alloys. Despite these new processes, practically all ferromanganese was produced in blast furnaces during the first half of the 20th century.

Burning of coke is the primary source of energy in the blast furnace, and the coke consumption is about four times as high as in the electric furnace. Because of the high cost and scarcity of blast furnace coke and the relatively lower capital investment in electric furnaces, a large number of blast furnace plants have been closed down over the last decades, whereas the production of ferromanganese in electric furnaces has increased. The electric furnace is also much more flexible, in that slag can be reprocessed in the silicomanganese process. In 2005, approximately three-quarters of the world production was in electric furnaces and the rest in blast furnaces.

A plant in Norway (Tinfos, Øye Smelteverk) for production of manganese alloys is shown as Figure 1.1.



Figure 1.1 A plant in Norway for production of manganese alloys (Tinfos, Øye Smelteverk).
Photo: Leif Hunsbedt

Chapter 2

Alloy specifications and uses

2.1 Alloy specifications

The primary use of manganese is in the steel industry where manganese is added mainly in the form of ferroalloys. Several different types of manganese alloys are marketed. These alloys may be divided into four major groups:

- High carbon ferromanganese, normally with *c.*78% Mn and *c.*7.5% C.
- Refined ferromanganese with carbon content ranging from 1.5% C down to 0.5% C.
- Silicomanganese with silicon content normally from 17% to 20%, corresponding respectively with carbon contents from approximately 2.0% down to 1.5%.
- Low carbon silicomanganese with 26–31% Si and carbon content from 0.5% down to 0.05%.

The number of alloy specifications is large. Some suppliers list more than 20 different products. The alloys vary in manganese, carbon, silicon, phosphorus, and even nitrogen content. Because of the scarcity of low phosphorus manganese ores, many users, especially alloy steel manufacturers, will pay a premium for low phosphorus alloys. Typical examples of alloy specifications for standard high, medium and low carbon ferromanganese alloys and for standard and low carbon silicomanganese are shown in Table 2.1.

Table 2.1 Typical manganese alloy specifications (wt.%).

Grade	Mn	C	Si	P	S	B (ppm)
HC FeMn	78	7.5	0.3	0.20		
MC FeMn	80-83	1.5	0.6	0.20		
"	80-83	1.0	0.6	0.20		
LC FeMn	80-83	0.5	0.6	0.20		
SiMn	67	1.7	17.5	0.10	0.02	200
"	67	1.5	17.5	0.10	0.02	200
"	68	2.0	17-20	0.15	0.02	200
LC SiMn	60-63	0.5	25-27	0.10	0.01	100
"	59-63	0.1	26-30	0.10	0.01	100
ULC SiMn	58-62	0.05	27-31	0.05	0.01	100

2.2 Impurities in Mn alloys

The trend towards production of higher quality steels with lower impurities increases the pressure on producers of manganese alloys to improve the quality of their products by tighter specifications on harmful elements – particularly carbon, sulphur and phosphorus. Commercial production of manganese alloys from ordinary raw materials inevitably introduces many impurities in the final metal, although in smaller amounts. Typical concentrations of a number of these constituents are given in Table 2.2.

Table 2.2 Typical concentration of impurity elements in manganese ferroalloys.

Alloy/grade	wt.-%			ppm												
	P	O	N	Al	Ca	Mg	Ti	Cr	Co	V	Ni	Cu	Zn	S	B	H
HC FeMn	0.18	0.2	0.03	50	100	300	80	200	220	400	220	130	80	20	< 5	20
MC FeMn	0.17	0.4	0.12	50	100	0.30%	40	350	270	400	280	150	10	40	< 5	15
LC FeMn	0.18	0.4	0.12	50	100	0.20%	50	750	290	450	280	170	10	30	< 5	15
VLC FeMn	0.18	0.4	0.13	50	100	0.20%	50	1200	290	450	280	170	10	30	< 5	15
MC SiMn	0.08	0.15	50ppm	150	200	350	0.20%	320	110	250	300	75	15	90	220	15
LC SiMn	0.05	0.15	50ppm	150	100	200	0.25%	300	70	250	300	75	15	30	220	15

Source: Hoel (1998)

2.3 Uses of Mn alloys

Since about 90% of all manganese produced is consumed in the steel industry, the world demand for manganese depends directly on the needs of the steel industry. There are numerous grades of steel and each grade requires a different amount of manganese. The average unit consumption of manganese per ton of steel is currently about 7.5 kg in the industrialized countries.¹ For constant unit consumption, manganese demand follows the growth in steel production. The world crude steel production was 1130 million tons in 2005.²

The bulk production of steel is multi-purpose low carbon steel containing from 0.15% to 0.8% manganese. A large part consists of low carbon steel sheets with less than 0.3% manganese. High strength steels, representing 3–4% of the tonnage of steel produced, contain more than 1% manganese. Steels containing 13% Mn or more have unique properties which make them indispensable for applications where great toughness and wear resistance are required, for example in gyratory crushers, jaw-crusher plates and teeth for earth-moving equipment, etc.³

Stainless steels which represent less than 2% of total world steel production primarily make use of chromium and nickel as alloying elements, but they also contain *c.*1% manganese. In fact, nickel can be partly or entirely replaced by manganese in stainless steel, giving a manganese content of 4–16%. These steels are not yet produced in large quantities but they could increase in the future depending on the development of the price of nickel compared to that of manganese.

There is some direct consumption of manganese ores and sinter in the blast furnaces where pig iron is produced, but manganese is mainly consumed in the form of ferro-manganese, silicomanganese and manganese metal. Only about 5% of the manganese used in steel production is introduced into the blast furnace. The manganese content in pig iron is only a small part of the total requirement for steel production. The main addition of manganese takes place as the manganese alloys or manganese metal are added, just after the final step in the steelmaking process or during alloying in the production of more highly alloyed steels.

The total world production of manganese alloys was *c.*10.4 million tons in 2004, which represented 14 % increase from 2003. This production figure includes 3.55 million tons of high carbon ferromanganese, 5.9 million tons of silicomanganese, and 0.93 million tons of medium and low carbon ferromanganese.⁴ The last years increase

¹ MHRP, Manganese Health Research Program, <http://www.manganese-health.org/background/production>.

² International Iron and Steel Institute, www.steelnews.com06/jan/jan62.htm

³ International Manganese Institute, http://www.manganese.org/imni2/about_mn4.php3.

⁴ Robinson, I. 2006. *Manganese*. www.mmta.co.uk/economicsFacts/Articles/MiningJournalReview/Manganese.pdf

is mostly due to high production in China, which in 2004 accounted for 44 % of the world production.⁵

Crude steel is produced by refining pig iron, scrap iron, and direct reduced iron (DRI). Most crude steel is produced either in the basic oxygen furnace or in the electric arc furnace. Only a small part is still produced in open-hearth furnaces and an even smaller part in Bessemer converters or by other processes.

Manganese is added to steel for several reasons:

- to influence strength, toughness and hardness as an alloying element
- to combine with and remove sulphur
- to control the morphology of sulphides
- to act as deoxidizer.

Of particular interest is the modifying effect of manganese on the iron-carbon system by increasing the hardenability of the steel. Iron crystallizes at room temperature into alpha iron (ferrite) which is a body-centred cubic structure. At temperatures above 910°C, the structure transforms into gamma iron (austenite) which is a face-centred cubic form. As the steel is cooled down, carbon dissolved in austenite precipitates as iron carbide (cementite), and the austenite transforms into ferrite. Together, cementite and ferrite precipitate in a characteristic lamellar structure known as pearlite.

The important effect of manganese is to lower the temperature at which austenite transforms into ferrite, thus avoiding cementite precipitation at ferrite grain boundaries, and also to refine the resulting pearlitic structures. The strength and toughness of steel depend on the grain size and the volume fraction of pearlite. Alloying elements, including manganese, contribute to some solution hardening of the ferrite, but this effect is limited compared to that of carbon, nitrogen, phosphorus and even silicon. When the cooling process is accelerated by quenching, austenite transforms into structures with high strength, such as bainite and martensite.

Manganese improves the response of steel to quenching through its effect on the transformation temperature. Manganese is also a weak carbide former. Both properties are advantageous in heat-treated steels. Another important property is that manganese, like nickel, stabilizes the austenite in steel. Since manganese is not as powerful as nickel in its ability to stabilize austenite, more manganese is required to achieve the same effect. However, manganese has the advantage of being much less expensive. The effect of manganese in forming austenite can be reinforced by combining it with nitrogen, which is also an austenite-forming element.

⁵ Li, Y. *China Mn Industry Overview*, International Manganese Institute. China www.manganese.org/admin/

Crude steel contains undesirable amounts of sulphur and oxygen. In this respect, manganese plays a key role because of its ability to combine with sulphur. Its reaction with residual sulphur to form manganese sulphide avoids hot shortness of the steel and prevents interstitial liquid formation of iron sulphide. Of the manganese added to steel, about 30% is added because of its properties as sulphide former and deoxidant, while the other 70% is added purely as alloying element.

Silicon is the primary deoxidizer and is also an alloying component in some steels, for example in spring steel. Manganese is a milder deoxidizer than silicon and aluminium but enhances their effectiveness due to the formation of stable manganese silicates and aluminates. Silicomanganese is a more effective deoxidizer than individual addition of ferrosilicon and ferromanganese. Deoxidation with silicomanganese results in cleaner steel as the liquid manganese silicate formed coalesces and thus separates more easily from the melt, compared to solid SiO_2 formed during ferrosilicon deoxidation. This feature also reduces the problems with nozzle clogging during casting.

Steel makers have commonly used a mixture of high carbon ferromanganese and ferrosilicon to cover the need for manganese and silicon in their processes, but a trend towards more use of silicomanganese is observed. The bulk of manganese consumption in electric arc furnace (EAF) steel production is in the form of silicomanganese. The use of silicomanganese is expected to advance at a faster rate than high carbon ferromanganese consumption. Silicomanganese adds less phosphorus, carbon, aluminium, and nitrogen to the steel compared to a mixture of standard high carbon ferromanganese (HC FeMn) and ferrosilicon with 75% Si (FeSi75). Standard quality silicomanganese (SiMn) is used in most silicon and manganese containing steels where the combination of carbon, manganese, silicon, and trace elements fits the final steel analysis in an economical way.

Medium and low carbon ferromanganese is used in steels where the carbon content must be controlled and cannot be reduced after the addition of the ferroalloy. Low and medium carbon grades (0.5%–1.5% carbon) are mainly produced by oxygen refining of high carbon ferromanganese. Low and medium carbon alloys can also be produced in a silicothermic process involving reaction between silicon in silicomanganese alloy and manganese ore (Chapter 9). The silicothermic process is still in use some places, especially for production of the lowest carbon grades. The consumption of refined alloys with reduced carbon content is increasing due to increasing production of low carbon steels. In 2004, the worldwide production of refined ferromanganese (< 2% C) was 0.925 million tons.⁵

Electrolytic manganese is the purest form of manganese and has a minimum content of 99.9% Mn. It is used in the production of aluminium and copper alloys, for special grades of stainless steel and other special steels, and for electronic applications. Approximately 150000 tons of electrolytic manganese metal was produced in the year 2000.

Low carbon and ultra low carbon silicomanganese (LC SiMn and ULC SiMn) improve the productivity in the manufacture of stainless steel and special steel by eliminating decarburization in the final step. The use of low carbon silicomanganese in stainless steels and alloy steels provides a more economical production route, where a combination of manganese and silicon is required in a low carbon steel product.

Aluminium alloys constitute the largest non-ferrous metallurgical use of manganese. Manganese improves the corrosion resistance of aluminium. Aluminium alloys with a Mn content of 1% or more are widely used in beverage cans and in food handling equipment. Manganese bronzes are copper-based alloys, strengthened by small additions of manganese (up to 4.5%). These alloys are used for marine propellers and fittings, and gears and bearings.

There are also some non-metallurgical applications of manganese. The largest non-metallurgical market is for potassium permanganate, manganese sulphate, manganous oxide, manganous chloride, and for manganese dioxide in dry cell batteries. Potassium permanganate is a potent oxidizer and is used in chemistry and medicine as a disinfectant agent.

Chapter 3

Raw materials

3.1 Manganese ores

3.1.1 Mineralogy

Manganese occurs in nature in form of minerals. More than 300 minerals are said to contain some manganese, but only a small number have a high manganese content and these minerals are the main constituents in the most important ores. The manganese mineralogy is complex since manganese occurs in divalent, trivalent and tetravalent states. The most common manganese minerals are oxides, carbonates and, less frequently, silicates and sulphides. Various other minerals may also be present in the ore, such as phosphates, arsenates, borates, etc. Because of the variable state of oxidation, a number of the manganese oxides incorporate large alkali or alkaline-earth ions (K^+ , Ba^{2+}) in their lattice (Ostwald 1988). Consequently, manganese ores for industrial use contain a lot of foreign and unwanted elements. Some of these elements cannot be removed in the mining and ore dressing stages.

In the majority of ores, manganese is found in the tetravalent state as oxides or hydroxides. Their formation involves absorption of oxygen in the air, and consequently such ores are linked with geological phenomena near to the earth's surface, such as erosion, sedimentation and volcanism. Pyrolusite (MnO_2) and cryptomelane (KMn_8O_{16}) are the most important tetravalent manganese minerals. Psilomelane (= romanechite) comes next (Ostwald 1988). This is an amorphous hydrated oxide with mixed manganese valency and normally with varying contents of barium and potassium oxides.

Manganese minerals of significant abundance and economic importance are listed in Table 3.1. Braunite and braunite II are common complex silicate minerals usually occurring in association with bixbyite, hausmannite and pyrolusite in deposits such as the Postmasburg and Kalahari manganese deposits of South Africa where braunite is the principal manganese mineral. Rhodochrosite is a common carbonatic mineral in various ores.