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ON THE ROLE OF FERROALLOYS IN STEELMAKING

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ABSTRACT

Ferroalloys are added in steel to improve properties like tensile strength, ductility, fatigue strength and corrosion resistance. Additionally, there can be several other tasks for ferroalloys like in refining, deoxidation, control of non-metallic inclusions and precipitates. The short history of ferroalloys is introduced parallel to the development of different steel types. Then the latest innovations like development of new low- and high-alloyed (HSLA and stainless) steels are discussed. Influences of ferroalloys and special requirements in different stages in steelmaking process from melting to casting are considered.

The eventual influence of oxide impurities in ferroalloys to steel cleanliness was examined. It was observed that concerning primary alloying in early stage of ladle treatments the influence of ferroalloys is hardly decisive. Trimming additions close to casting start are more critical but on the other hand the additions are quite small and thus do not markedly influence the steel composition. However, the possible risk of ending up macro-inclusions to solidifying steel should be considered. Finally, some novel potential developments of ferroalloys as master alloys carrying nanoparticles are discussed.

KEYWORDS: Ferroalloys, production, low-alloyed steels, high-alloyed steels, stainless steels, influence on steels properties, refining, deoxidation, oxide inclusions, precipitates, nanoparticles.

1. SHORT HISTORY OF FERROALLOYS

The history of ferroalloys is relatively short if compared to that of iron and steel. Ancient iron artefacts were of fairly pure iron containing only carbon as a significant alloying element. That was self-evident as the steel was produced via direct reduction route in bloomery-type furnaces at so low temperatures that iron was formed in solid state and other components like manganese and silicon which are typical in modern steels were found only as slag inclusions in steel. Occasionally, iron could contain such easily reducible elements like Ni and Cu originating from ores or in the case of nickel even from meteoritic iron [1]. When bigger shaft furnaces were developed with stronger air blasting through tuyeres, temperature in the combustion zone was increased, and iron could dissolve more carbon and melt: thus the blast furnace process was discovered. This progress took place in the late Medieval Age in Central Europe. The product was carbon-saturated cast iron which typically contained a few percents of silicon and eventually also some manganese depending on the ore composition. Pig iron from blast furnaces was used as foundry iron for castings or converted to steel by difficult and time-consuming refining process. Such processes were gradually developed but bloomery steel kept its dominance until the 19th century.

Two centuries ago there were two main methods to refine hot metal from blast furnaces to steel. They were puddling with oxidizing flame in a reverberatory furnace and the crucible process in which iron oxide (ore, scale) was added in hot metal to react with carbon and to get low carbon
Principal some alloying would have been possible but there were several prerequisites before a rational alloying could be carried out. Firstly, the breakthrough inventions in chemistry in the end of 18th and early 19th century with discovery of elements (like nickel, oxygen, manganese, chromium, molybdenum, silicon from 1751 to 1824) and understanding of chemical reactions like combustion/oxidation and reduction made it possible also to recognize essential events of contemporary iron and steelmaking processes and to start developing new processes [3]. Secondly, there should be some evidence of beneficial influences of additions on steel properties. This means understanding of steel microstructure and its relations to steel properties and further to influencing mechanisms of alloying elements. Thirdly, it should be possible to produce potential alloying materials at a reasonable price. During the second half of 1800s these prerequisites gradually began to be fulfilled.

In steelmaking the decisive breakthrough was the invention of converter process by Henry Bessemer in 1855. He developed the idea to blow air inside the carbon-rich hot metal and thus burn with oxygen the carbon dissolved in iron melt. He also succeeded to elaborate a proper reactor and technology for Bessemer process. First Bessemer converters were lined with acid silica lining. Even it could operate at temperatures up to 1600°C but the lining life was short. Due to acid environment the slag was silica-based and thus unsuitable for phosphorus removal. This was a big problem at that time in the Great Britain, where P-bearing iron ores were common. The problem was solved by S.G. Thomas and P.C. Gilchrist who succeeded to develop basic doloma lining introduced in 1878-1879 [4]. Doloma is a calcia-magnesia mixture obtained by burning natural dolomite mineral, (Ca,Mg)CO₃. Basic Thomas converters gradually replaced acid Bessemer converters. Another process route was the open hearth process (reverberatory furnace heated by flame) developed by Siemens and Martin brothers in 1860-70. Open hearths became popular as they used oil as fuel for heating and melting and thus were able to receive liquid hot metal and solid scrap in any ratio in the charge. First of them had acid lining, but basic lining and the new steelmaking practice were adopted as well. Basic lining was available also for electric furnaces when they were started to use for steelmaking in the beginning of 1900s and for ferroalloys production too.

In parallel with Bessemer’s process development, Scottish metallurgist Robert Mushet added manganese-containing “spiegelisen” in liquid steel to “kill” it, to prevent “wild boiling” caused by carbon-oxygen reaction and CO gas formation. Manganese was thus used for steel deoxidation. Also the beneficial effect to avoid hot shortness by binding excess sulphur was soon recognized [1]. Spiegelisen containing 8-15 % Mn and ¬5 % C was produced already in the 18th century in blast furnaces. Mushet was also one of those who developed first “tool steels” with 1-2 % Mn in 1860s. Robert Hadfield invented work hardening steel in the 1880s with 11-14 %Mn and 1 %C [1]. This “Hadfield steel” has still a firm position in impact- and wear-resistance type applications.

At that time metallurgists started to consider addition of alloying elements to steel in a form of a ferroalloy - an alloy of iron with at least one another element except carbon. Production of ferroalloys was, in general, much easier and more economic than to make pure elements (Mn, Cr, Si, Ti, V, W...) but even the product was more practicable for alloying due to lower melting temperature. Small scale production of ferroalloys was started in 1860s by using crucible process. Chromium ore were reduced by coal in graphite crucibles which were heated to high temperatures to get liquid high carbon alloy with ¬25 %Cr. High-Mn ferromanganese production (80% Mn and 6-7%C) was started in a French blast furnace in 1877. It was also demonstrated that FeSi could be produced in a blast furnace, as well as low content FeTi and FeV. On the other hand production of FeCr in the same way was found difficult due to high melting point of the slag formed during smelting [5]. When electric furnace technology was introduced at the end of 1800s, electric smelting of ferroalloys gradually progressed in early 1900s and nowadays all ferroalloys which require furnace technology are being produced exclusively in electrical furnaces.
The occurrence of silicon in iron has its historical origin in blast furnace iron production. Relatively high Si contents (several percents) could be obtained in pig iron which was used in foundries as grey cast iron where Si promotes graphite formation and improves ductility. Swedish chemist Jacob Berzelius produced a kind of ferrosilicon in early 1800s by crucible reduction. He also succeeded to separate elemental silicon in 1824 [3]. Production of elemental silicon turned to be very difficult whereas ferrosilicon was easier to produce. In blast furnaces it was possible to produce hot metal up to 20 % Si in the late 19th century. The product was used for steel deoxidation and alloying. When electric furnace technology emerged it was soon applied for FeSi production too. In ferroalloys production furnaces were designed to operate in submerged arc mode (SAF) in which the high resistivity of the charge is utilized for smelting.

2. ADVANCEMENTS IN STEELS AND RELATIONS TO FERROALLOYS

As mentioned, ancient iron artefacts were made of almost pure iron containing only carbon as the only alloying element. Properties like hardness, strength and toughness were controlled by changing carbon content by carburizing or decarburizing treatment which skills were owned by blacksmiths. Historical “super steels” like “Damascus”, “Bulat” and “Tatara” steel had such amazing properties which are difficult to attain with modern technologies. In these steels properties were based on sophisticated processing with combination of high and low carbon materials, which formed a composite layered structure via forging–folding–welding, tens or hundreds of times [6, 7].

Generalized steel alloying was not possible until the 19th century. When the understanding of basic chemistry progressed, it became possible to analyze steel composition. At the same time great advancements were attained in materials characterization. By optical microscopy the microstructure of steel was revealed and relations found between the composition, microstructure and properties. H.C. Sorby in Sheffield pioneered in this field. The value of metallography was generally stated by 1885 [1]. Heat treatments of steels were developed and different polymorphic forms and micro-structures of iron were identified (austenite, ferrite, pearlite, cementite, martensite and later bainite in the 1920s). Invention of electron microscopy in 1930s further improved knowledge about steel structure and phenomena influencing the relations with the properties. In table 1 above the role of different common alloying elements in steels have been collected.

In most steels carbon is still the base element influencing the structure but by adding different alloying elements formation of microstructures and their properties can be controlled in much wider range. Alloying elements can act in several ways in steel. Common mechanisms are solid solution strengthening and precipitation hardening. The first one is based on the influence of substitutional atoms which causes stress field in the iron lattice. On the other hand precipitation hardening is based on formation of new precipitated phases like carbides (dissolved carbon reacts with Cr, Mo, Ti, Nb, V, W etc), nitrides (dissolved nitrogen reacts with Al, Nb, Ti, V) or carbo-nitrides [8]. Tiny precipitates can act as nuclei for new grains in phase transformation and further block grain boundaries preventing from grain growth. In low carbon steel certain inclusions can act as nuclei for acicular ferrite formation with improving effects on steel properties. In latest decades improved knowledge of thermodynamics, kinetics and mechanisms of precipitates formation and phase transformations in different steels has been as basis to create new steel grades and manufacturing methods. Heat treatment processes have strongly evolved as well. Thermo-mechanical controlled rolling process is one example which can produce better mechanical properties in steels with less alloying but cheaper and faster process route [9].

The production of steel has increased rapidly during the last two decades from the level of 700 Mt/a in 1980-90s to the current level of 1400-1500 Mt/a. The biggest growth has been in China; also India and other developing economies (Brazil, Russia) have increased production. The production of major ferroalloys follows roughly the growth of steel although a trend has been
towards minimizing the alloying in steels in accordance with the principles of “lean manufacturing”. The share of e.g. micro-alloyed steels has increased markedly. On the other hand stainless steel production has grown surprisingly. Progress of stainless steel is presented together with ferroalloys in figure 1 (left) and comparison of major ferroalloys (right). SiMn seems to have the fastest growth; it has partly replaced FeMn and retarded the growth of FeSi production too. FeCr has made a fast growth too due to the expanded stainless steel production.

Table 1: Common alloying elements in steel, their influences and applications

<table>
<thead>
<tr>
<th>Alloying element</th>
<th>Influence on structure</th>
<th>Influence on properties</th>
<th>Typical applications in steels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>Austenite forming, substitutional atom, carbide stabilizer</td>
<td>Increases harden-ability, strength, toughness, hot workability</td>
<td>Deoxidation with Si (Al), forms MnS, alloying element in low-alloyed steels up to 1.6%. Hadfield steel 13%Mn, AISI 200 series stainless 5-10%Mn</td>
</tr>
<tr>
<td>Cr</td>
<td>Ferrite forming, substitutional atom, forms carbides</td>
<td>Increases hardenability, strength, corrosion resistivity</td>
<td>In low-alloyed steels up to 2%Cr, in stainless steels 11-25%. Heat resistant steels, tool steels</td>
</tr>
<tr>
<td>Ni</td>
<td>Austenite forming, substitutional atom</td>
<td>Increases strength, toughness, impact &amp; corrosion resistance</td>
<td>Case hardening steels up to 3.5%Ni Stainless steels 8-20%Ni Heat-resistant alloys ~25%Ni</td>
</tr>
<tr>
<td>Si</td>
<td>Ferrite forming, substitutional atom</td>
<td>Ferrite hardening</td>
<td>Deoxidation; slag reduction; typically 0.3-0.6%Si. Spring steels 1.7-2.2%Si Electrical Si-steels 1-4%Si</td>
</tr>
<tr>
<td>Cr, Mo, WTi, Nb, V</td>
<td>Carbide formers</td>
<td>Increase hardness, strength, wear resist</td>
<td>Tool steels, wear resistant steels</td>
</tr>
<tr>
<td>Nb, Ti, V Ta,(B),Al</td>
<td>Nitride formers Grain refinement</td>
<td>Increase strength and ductility</td>
<td>Fine-grained steels; High strength low alloyed HSLA steels</td>
</tr>
</tbody>
</table>

Figure 1: Growth of the World production of Stainless steel and Ferroalloys (left) and comparison of FeMn, SiMn, FeSi and FeCr (right) [10, 11]

3. IMPURITIES IN FERROALLOYS

Ferroalloys have a high content of the major component, typically 50-90 %, the rest being mostly iron (Fe) and more or less “residues” of reductants used in ferroalloy production (carbon, aluminum, silicon depending on the process). How these components are limited in ferroalloys
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depends on the targeted analysis range. Such metallic impurities like Al, Ca, Mg, Ti, V etc can have special limitations due to their influence on oxide inclusions or other precipitates (nitrides, carbides). Finally, ferroalloys contain small amounts of impurities S, P, gases (O, N, H) and moisture. In this paper we pay attention to oxygen and its eventual influences in steelmaking. Very little information is available about the O and N contents and their existence in ferroalloys. Some data were collected in table 2.

Table 2: Analyzed oxygen and nitrogen contents in some ferroalloys [12, 13, 14, 15]

<table>
<thead>
<tr>
<th>Fe-alloy</th>
<th>Type</th>
<th>O, ppm</th>
<th>N, ppm</th>
<th>Inclusions found</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeMn</td>
<td>HC 6-8 % C</td>
<td>1500</td>
<td>5200</td>
<td>3500</td>
<td>30, 80, 40</td>
</tr>
<tr>
<td></td>
<td>MC max 1.5 % C</td>
<td>100-1200</td>
<td></td>
<td>600-700</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LC &lt; 0.5 %C, 0.2%Al</td>
<td>400, 11100</td>
<td>400, 1400</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>LC &lt; 0.5%, 0.2%Al</td>
<td>60, 240</td>
<td>780</td>
<td>50, 70, 150</td>
<td></td>
</tr>
<tr>
<td>FeSi</td>
<td>75 % Si, &lt;0.5 % Al</td>
<td>310, 780</td>
<td>290</td>
<td>7</td>
<td>CaO, MgO, Al2O3</td>
</tr>
<tr>
<td></td>
<td>-&lt;; &lt;1 % Al</td>
<td>1000</td>
<td>(60-3000)</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-&lt;; &gt;0.5 % Al</td>
<td>160</td>
<td></td>
<td>-</td>
<td>Al2O3, CaO</td>
</tr>
<tr>
<td></td>
<td>65 % Si; 2 % Al</td>
<td>1700</td>
<td></td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>FeCr</td>
<td>HC 60 % Cr, 7.5 % C</td>
<td>200</td>
<td>200</td>
<td>Al2O3; nitrides</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>HC LP</td>
<td>2100</td>
<td>430</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The values from the literature were rounded up as there is a large scatter in parallel analyses.

In some ferroalloys the oxygen content is quite high, thousands of ppm even up to wt-% level (LC FeMn). There is a general tendency that oxygen content increases if the ferroalloy has some oxidizing refining [13,16]. The table shows also types of inclusions which were found in ferroalloys. It is quite natural that MnO and MnS inclusions were found in FeMn. Correspondingly, presence of silicates in FeSi is self-evident. Other oxides observed (CaO, MgO, Al2O3) originate from impurity oxides in primary raw materials or can be formed as secondary oxidation products in the ferroalloy.

What kind of effects can oxygen in ferroalloys have on steel? Simple estimation shows that if we add 1% ferroalloy containing 1% oxygen (1000ppm), we add 100 ppm O in the steel. That is very much indeed. Even the materials with >> 1000ppm Otot can be dangerous if added big amounts when the oxygen addition is tens of ppm. In primary alloying such additions have no influence as the ordinary deoxidation is performed and the inclusions have enough time to form and transform, and to separate from the liquid steel during ladle treatments. More critical are the trimming additions made in a late stage of secondary steelmaking just before casting. Then there is only little time to eliminate the influences and traces of oxides migrated into the steel via the ferroalloy addition.

4. THERMODYNAMIC CALCULATIONS TO EVALUATE EVENTUAL INFLUENCE OF OXIDES IN FERROALLOYS

In order to clarify the eventual “minor” effects of ferroalloy additions in steels calculations were performed by applying FactSage 6.2 Program Package, FT-oxide and FACT databases [17]. A general observation was that the contents of oxygen and even oxides are so small that they have very little influence on the steel chemistry. This conclusion concerns “trimming” additions i.e. max 0.1% of the certain ferroalloy is added. Increase of oxygen is then on ppm level. When alloying additions are much higher, then for instance FeMn additions can cause remarkable increase of Otot content in steel, influence of which can last long time as FeMn lumps are relatively slowly melting.

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The same may concern FeCr. Considering the oxide inclusions in steel also other impurities (than oxygen) in the ferroalloy can have influence. Aluminum is a very strong deoxidizer and therefore it can easily form alumina inclusions and react with other inclusions already existing in the steel.

As an example the influence of FeSi addition to C/Si/Mn steel used for wire production is discussed here. The steel is deoxidized with Si and Mn and the special requirement is that only deformable silicate inclusions are allowed in the final steel. The basic steel composition was 0.6 % C, 0.25 % Si, 0.65 % Mn, 0.001 % Al, 30 ppm Otot, 1 ppm Ca, Mg. The calcium and magnesium contents originate from the slag when the steel was equilibrated with small amount of slag (45 % CaO, 33 % SiO2, 17 % Al2O3, 5 % MgO). Thus the oxide inclusions in steel were related to those used to be in industrial steel production. In figure 2 it is seen that without any FeSi addition the [Al] and [O] contents are 10 and 29 ppm, respectively. Further, there is little “slag” or liquid inclusions containing the four oxides mainly. When FeSi with 1 % Al and 0.1 % O is added, Al content and liquid oxides in steel increase whereas oxygen content slightly decreases due to the effect of Al. When the addition exceeds 0.06 % Si, solid oxides, spinels and Ca-Mg-Al-silicates start to form, which gradually replace liquid oxides. The increase in Al2O3 in “slag” indicates the transfer to precipitation of solid and is related to the rise of Al-content as well. This phenomenon would be quite detrimental to the properties of the case steel.

![Figure 2: Influence of FeSi-1%Al-0.1%O addition on oxygen and Al contents in steel and formation of liquid and solid oxides. Mn/Si deoxidized steel in the presence of CaO-SiO2-Al2O3-MgO slag](image)

The case study above was based on calculations of thermodynamic equilibrium in the system. It also showed that when operating inside certain “safety limits” the influences of ferroalloys impurities to oxide cleanliness of steels are minor. Another approach is to look at the actual inclusions in ferroalloys (table 2) and to think about what will happen if they get into steel in very late stage of the process. Then it is possible that the inclusions have not time to spread evenly and react to equilibrium. When macroscopic inclusions appear in the ferroalloy they can end up to the final solid steel. This is rather rare but possible, anyway.
5. FUTURE TRENDS AND POTENTIALS FOR FERROALLOYS

From steelmakers’ viewpoint optimal usage of ferroalloys is a quite complex problem. It is not enough to “buy” the major element(s) but to consider also the minor components and impurities. Often the selection of steel grades is numerous and a wide variety of alloys would be desirable. For practical reasons e.g. silos the number of alloys must be limited. Therefore compromises must be done. Other important aspects – not discussed here – are the physical properties, lump size, shape, amount of fines etc which are essential in melt shops. Concerning trimming additions a growing technique is wire feeding which has higher material cost but several benefits. The yield and scatter/hitting ratio are extremely important and have a great economical impact too. A thorough investigation of ferroalloys usage, practices, special requirements and optimization should be worth of execution.

As discussed earlier small precipitates play a decisive role in precipitation hardening and grain refinement which are powerful strengthening mechanisms in steel. These precipitates are typically nitrides or carbides. Even small oxide inclusions have been stated to have similar effects; they can promote nucleation of acicular ferrite in low carbon grades and hinder grain growth thus leading to grain refinement. Typical such particles are for instance Ti- and Ce-oxides [18, 19]. Conventionally, this kind of inclusions are endogenous i.e. they are formed in situ in the steel matrix. In proper circumstances they are formed and remain with optimal size and distribution. Another principle has been proposed: to prepare such micro- or nanoparticles ex situ and add them into steel before casting. Direct adding of nanoparticles into melt is difficult and a carrier is desired. A very potential way is to use a ferroalloy as the carrier. Such a “master alloy” should contain orders of magnitude higher density of the particles than which is aimed in the steel to compensate the dilution effect in alloying. Several techniques have been proposed to prepare master alloy e.g. by mixing nanopowder with alloy powder and making pellets, briquettes or cored wire, by adding nanopowder in liquid ferroalloy in casting and rapid solidification as well as by controlled generation via reaction and precipitation of particles in the master alloy [20, 21, 22].

6. CONCLUSIONS

The history of the utilization of ferroalloys exceeds only about 150 years back. Since that the production technologies for ferroalloys have developed and great variety of alloys specified for different steel grades have become available. The usage has strongly extended for diverse purposes including refining, alloying for improved strength, hardness, ductility, corrosion resistivity etc. During the last few decades micro-alloyed steels have emerged and grown faster than the conventional low-alloyed steel grades. On the other hand production of stainless steels has grown still faster which can be seen especially in FeCr consumption.

The levels of impurities in ferroalloys vary greatly and the customers’ requirements depend on the steel grades and object of use i.e. the requirements are different for final trimming additions than for primary basic additions. Most metallic impurities as well as C, S and P are limited by distinct analysis limits whereas such components like Ti, Al, Ca, Mg, N which can have detrimental influences via formation of inclusions and precipitates can be more critical to control. That kind of optimization of ferroalloys for different steel grades and purposes would be a challenging task for model developers.

Recently, the eventual role of oxides and other inclusions in ferroalloys has been raised to debating. Survey of ferroalloy analyses, examination of mass ratios alloy/steel and equilibrium calculations showed that, in general, the amount of oxides (based on oxygen analysis) in alloys is on a moderate level and thus its effect is faded by other additions in primary deoxidation and alloying. Concerning trimming additions the requirement is more critical due to short time for equilibration
and removal of inclusions. On the other hand the additions are small and the maximal impact is on ppm level. A possible risk stems from eventual macro-inclusions and non-acceptable type of inclusions due to late additions.

In the future it is probable that the division to bulk and special alloys will be further confirmed. Customer-tailored alloys are even possible as value-added products. That sets additional challenges to producers concerning both raw materials selection, process driving and eventual refining treatments. A novel potential product for ferroalloys producers might be master alloys which could carry nanoparticles into liquid steel before solidification. The idea has been proved to function for certain particles but for emerging applications plenty of R&D is needed both by developers of steels and proper master alloys.

7. REFERENCES