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# SELECTIVE OXIDATION OF MANGANESE IN MOLTEN PIG IRON

## SELEKTIVNA OKSIDACIJA MANGANA V STALJENEM GRODLJU

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An examination of the process of selective oxidation for molten pig iron indicates the possibility of lowering the content of unwanted or harmful elements. This process makes it possible to achieve the optimum Mn content in pig iron (hot metal) without any oxidation of the other elements present, such as carbon, etc. Several variants of oxygen blowing with the addition of a slag-forming component were checked. The final element content in the hot metal depends on the initial Mn content, the oxygen blowing and on the added slag components. The lowering of the Mn content in the hot metal to the limit solves the problems of converter processing, lowers the slag quantity, increases the yield of steel by more 4 % and improves the steel-making process.

Key words: selective oxidation, hot metal, high manganese content

Analiza procesa selektivne oksidacije tekočega grodlja daje možnost, da odstranimo neželene in škodljive elemente. Proces omogoča, da dosežemo optimalno vsebnost mangana v surovem grodlju (vroča kovina) brez oksidacije drugih elementov, ogljika in drugih. Preizkušenih je bilo več variant vpihovanja kisika z dodatki za tvorbo žlindre. Končna vsebnost mangana v grodlju je odvisna od začetne vsebnosti, vpihovanja kisika in od dodatkov za žlindranje. Zmanjšanje vsebnosti mangana do meje rešuje probleme konvertorskega procesiranja, zmanjša količino žlindre, poveča izkoristek jekla za več od 4 % in izboljša proces izdelave jekla.

Ključne besede: selektivna oksidacija, grodelj, visoka vsebnost mangana

## 1 INTRODUCTION

Only in some countries metallurgists face the problem of a large content of manganese in molten pig iron (hot metal) of above 4.00 % [1,2,3,4,5]. The higher Mn content in hot metal during the oxidation, i.e., during steel-making, influences the formation of slag and causes serious problems for the technology. For this reason, the reaction between manganese and oxygen in hot metal is still being investigated. There are particular problems with hot metal that has a manganese content above 1 %. The process of manganese oxidation was investigated from the points of view of the reaction mechanism, the thermodynamics and the kinetics, and different conclusions were proposed. The majority of investigations were performed on hot metal with a low manganese content, below 1.00 %. Only rarely was the object of the examination some hot metal with a high manganese content, higher than 4 %, as the initial content. Only on the basis of investigations with a high manganese iron can the present misunderstandings and confusion about results be solved, with the condition that the effect of the method of introducing the oxygen into the hot metal on the evolution of reactions is also considered.

During the processing of hot metal with a high manganese content to steel, a large quantity of slag is obtained that decreases the yield and increases the splashing [5,6]. So far, no process for the selective oxidation of manganese from hot metal before pouring into a steel-making furnace was developed and attempts to decrease the manganese content in hot metal were not successful. In fact in Austria, steel-makers gave up on the use of iron ore with a high content of manganese [1,5]. In Russia and Bulgaria trials of the oxidation of manganese were not successful and it was only possible to produce FeMn from slag with a high percentage of MnO [3,4,7]. The treated hot metal had a low carbon content and was not suitable for the making of steel with less than 2.00 % of manganese.

New technical solutions and equipment for the processing of hot metal in a ladle offer the possibility of decreasing some harmful or unwanted elements with selective oxidation [6,7,8] before tapping the hot metal into the steel furnace. In this work we ordered the problem of lowering the manganese content, combining the introduction of oxygen with the use of an appropriate slag. Specifically, the influence of the addition of slag-forming oxides, especially $SiO_2$, was investigated. The performed experiments indicate that it was possible to decrease the manganese content in the hot metal from 4.00 % or more to below 1.00 at 1773 K.

In this article the metallurgical and technological aspects of the selective oxidation of manganese with oxygen and slag formation on a pilot-plant scale are presented that offer the possibility of applications on an industrial scale.

## 2 METALLUGICAL CHARACTERISTICS OF SELECTIVE OXIDATION

Selective oxidation has to be carried out only with a sufficient supply of oxygen as well as with a slag that is rich in $Fe_xO$. The multi-reaction equilibrium of the selective oxidation of manganese can be deduced using a suitable method; however, a more reliable method of calculation is based on the equilibrium principle and a change of the Gibbs' free energy of the formation of oxides ($\Delta G^o$) for different reactions. It is important to calculate the conditions for the selective oxidation of manganese with no change in the initial carbon content and with the minimal oxidation of silicon. For the three elements carbon, silicon and manganese, three equations can be written showing a mutual equilibrium between any of two, with only two independent equations. The equilibria for the systems Mn-C and Mn-Si are solved with numerical iteration.

It is assumed that the change of the manganese content for low and higher initial contents does not have corresponding changes in the decreasing part of the curves in **Figure 1**, especially for the case of the Mn–humpback [3,9]. The changes in the manganese content at the lower part of the curves at 1873 K do not occur below the of Mn–humpback in melts without carbon content and for hot metal melts with 4.00 % or more C at 1573 K [1]. This strengthens the importance of clarifying the mechanism of the reactions in the systems Mn–$\{O_2\}$ and Mn–$Fe_xO$.

It is assumed that the mechanism of the reactions of selective oxidation of manganese with oxygen in the presence of $Fe_xO$ slag components occurs as shown in **Figure 2**. It is important that in the processing the continuity of the reactions fields is maintained: 1 – initial reactions (1st field), 2 – transition reactions (2nd field) and 3 – stable reactions (3rd field). It is further concluded that oxygen blown into the field of the initial reactions (mark 1) can react with iron, silicon, manganese and carbon. On the base of the $\Delta G^o - T$ dependences it is possible to expect that at 1573 K only the manganese is oxidised. It is assumed that the oxidation of carbon is damped because of the influence of a ferro-static pressure deep into the melt. In the second field (number 2 in **Figure 2**), the formed $Fe_xO$ is reduced with silicon. It is assumed that additional reactions occur in the third field of permanent reactions (number 3). The process of selective oxidation of manganese is achieved with a transition through all three fields in **Figure 2**, only.

The $e_i^j$ values for the temperature of 1573 K are calculated by applying two approaches: from the obtained data or from values for 1873 K, considering the difference in temperature.

The calculation of the free energy $\Delta G^o$ at different stages of the manganese's selective oxidation leads to a

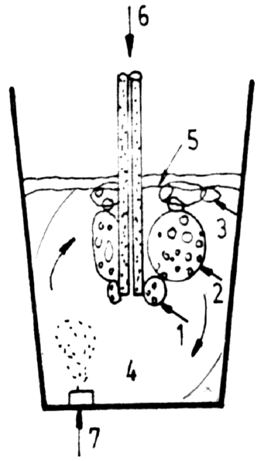


**Figure 2:** Mechanism of reaction blowing oxygen and slag components 1. initial reactions.; 2. transition reactions; 3. permanent reactions; 4. hot metal; 5. slag; 6. oxygen; 7. argon

**Slika 2:** Mehanizem reakcijskega vpihovanja kisika in komponente žlindre. 1 – začetne reakcije, 2 – prehodne reakcije, 3 – permanentne reakcije, 4 – tekoči grodelj, 5 – žlindra, 6 – kisik, 7 – argon

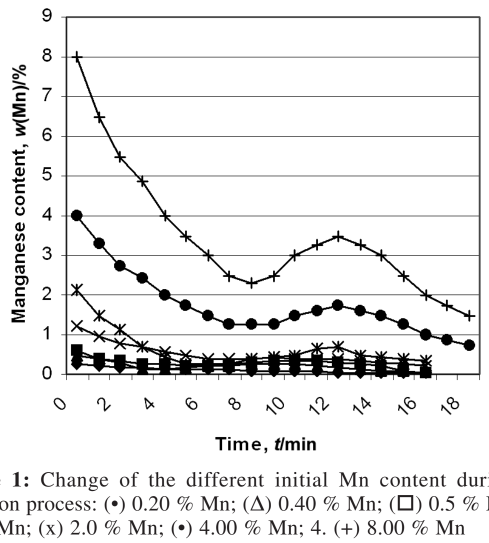


**Figure 1:** Change of the different initial Mn content during the oxidation process: (•) 0.20 % Mn; (Δ) 0.40 % Mn; (□) 0.5 % Mn; (x) 1.2 % Mn; (x) 2.0 % Mn; (•) 4.00 % Mn; 4. (+) 8.00 % Mn

**Slika 1:** Sprememba različne začetne vsebnosti mangana med procesom oksidacije: (•) 0.2 % Mn; (Δ) 0.4 % Mn, (□)0.5 % Mn, (x) 1.2 % Mn, (x) 2.0 % Mn, (•) 4.0 % Mn, (+) 8.0 % Mn

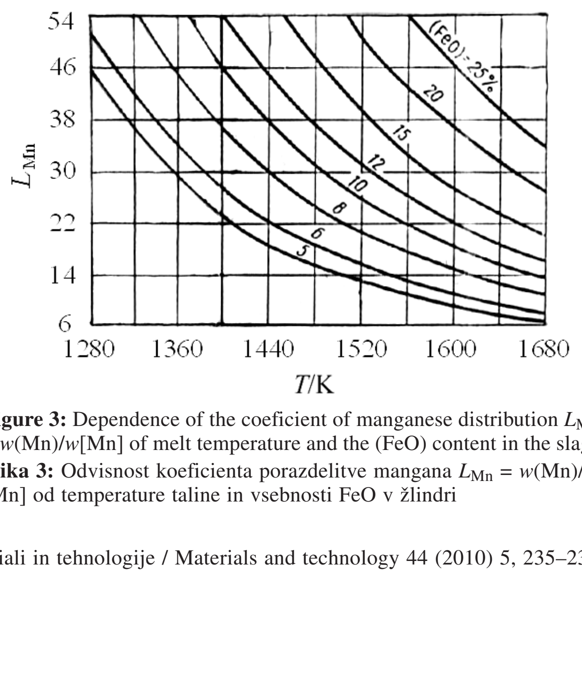


**Figure 3:** Dependence of the coeficient of manganese distribution $L_{Mn} = w(Mn)/w[Mn]$ of melt temperature and the (FeO) content in the slag

**Slika 3:** Odvisnost koeficienta porazdelitve mangana $L_{Mn} = w(Mn)/w[Mn]$ od temperature taline in vsebnosti FeO v žlindri different equilibrium situation. The possibility of prior silicon oxidation at 1573 K, thus, before the oxidation of manganese and carbon, is dependent on other influencing factors; firstly, of the slag composition. The equilibrium between the silicon and the manganese is reached at the beginning of the oxidation process and both elements are oxidized in parallel in preference to the carbon until the ternary equilibrium silicon, manganese and carbon is achieved. The content of carbon has to remain constant at the initial level or changed insignificantly. Thus, the final equilibrium composition of the hot metal depends not only upon the temperature and the initial composition, but also upon the activity of the oxides $a_{SiO2}$ and $a_{MnO}$.

## 3 THE OXIDATION OF MANGANESE, THE PRINCIPLE AND THE EXPERIMENTAL PROCEDURE

The solution to the problem of a high manganese content of about 4.00 % in the hot metal produced in Zenica could be found by considering the system Fe-Mn-Si-C-O at 1573–1673 K for $\Delta G^o - T$ dependences that offer the possibility of irreversible reactions. In this temperature range it is possible to achieve the value for the $w$[Mn]/$w$[C] ratio of 0.10, which allows the successful selective oxidation of manganese. The measure of the rate of accelerated reactions of manganese oxidation, which determines the degree of reaction, is the mass transport coefficient ($k_{Mn}$). A significant decrease in the content of one element ($X_1$) by a sufficient decrease of the second ($X_2$) can be achieved on the condition of $k_{X1} > k_{X2}$ and for the ratio of the distribution coefficient $L_{X1} > L_{X2}$. The most important is the distribution of elements, and especially manganese, between the hot metal and the slag ($L_{Mn} = w[Mn]/w(Mn)$) (**Figure 3**).

The experiments were performed in the ladle with a porous plug with a charge of hot metal with the composition in mass fractions: (4.03 ± 0.25) % C, (3.80 ± 0.52) % Mn and (0.56 ± 0.10) % Si. The oxidation was carried out with oxygen blowing and the addition of 6 % of $Fe_xO$ for the slag formation. The experiments were performed in three variants of the lance blowing of oxygen: 1. on the slag surface, 2. in the hot metal and 3. in the metal being rinsed with argon. The temperature of the hot metal was, in all cases, 1573 K.

For the existence of all three reactions fields, only the role of $Fe_xO$ as an oxidation intensifier and the control of the oxidation of silicon with the present component $SiO_2$ were assumed. If all the reaction fields are reduced to one field of permanent reaction, it would be difficult, or even impossible, to control the selective oxidation of iron, silicon, manganese, carbon, etc. The decrease of manganese content to the equilibrium value excludes it from the oxidation process and the content of manganese at the start of the oxidation of carbon and iron is considered as critical $[Mn]_c$.

## 4 EXPERIMENTAL RESULTS

The obtained experimental results show that the most successful manganese oxidation process occurs during the blowing of oxygen with parallel argon rinsing (variant 3) without the oxidation of carbon, and acceptable kinetics of silicon oxidation. Data on the oxidised quantity of manganese and the losses of silicon and carbon are presented in **Figures 4 and 5**. It is obvious that already after 7.5 min. of oxidation in the variant 3, the final manganese content of 0.10 % Mn was achieved with the oxidation rate of $v_{Mn}$ = 0.39 % Mn/per min, which is higher than that quoted rate of $v_{Mn}$ = 0.35 % Mn/per min [3]. With the variant 2, the final manganese content was <1.00 %. The slag with the optimal characteristics was obtained with the largest additions of $Fe_xO$ and $SiO_2$. In spite of the large oxygen supply, the average free oxygen content in the hot metal is (3 ± 2) µg/g.

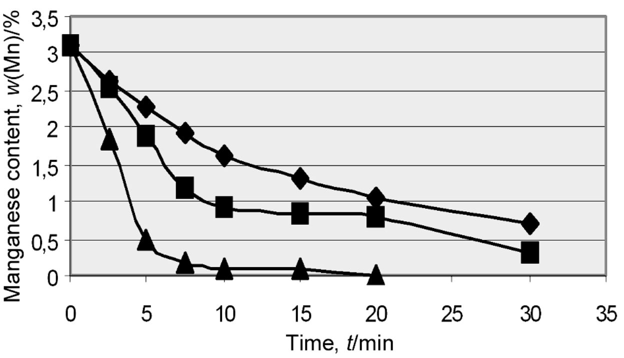


**Figure 4:** Oxidation of manganese at 1573 K for variants: 1. (◇) blowing on melt surface; 2. (□) blowing in melt; 3. (Δ) blowing in melt and rinsing through a porous plug

**Slika 4:** Oksidacija mangana pri 1573 K za variante: (◇) vpihovanje na površino taline, (□) vpihovanje v talino, (Δ) vpihovanje v talino in izpiranje z argonom skozi porozen čep

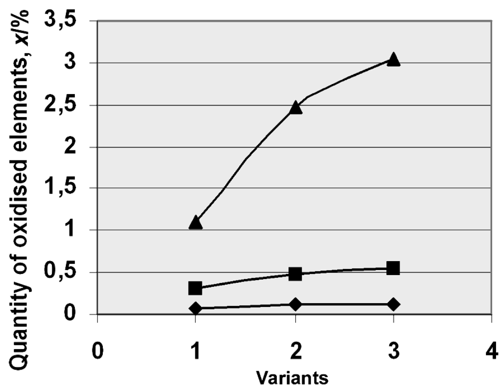


**Figure 5:** Average oxidised elements quantity of carbon (◇), silicon (□) and manganese (Δ) during oxidation for variants: 1 – blowing to surface; 2 – blowing into melt; 3 – blowing into melt with argon rinsing

**Slika 5:** Povprečna količine oksidiranih elementov ogljika (◇), silicija (□) in mangana (Δ) med oksidacijo mangana za variante: 1 – vpihovanje na površino, 2 – vpihovanje v talino in 3 – vpihovanje v talino z izpiranjem z argonom

In the hot metal at 1573 K, the oxidation of manganese alone is connected to the effect of the high carbon content and to interaction parameters with a value different to that at 1873 K. The composition and activity of slag formed with lance oxygen blowing on the melt top, in the melt, as well as for argon rinsing are different for the same slag addition. For instance, the activities $a_{MnO}$ and $a_{FeO}$ at 1573 K are for oxygen top blowing, 0.234 and of 0.642, into melt blowing, 0.395 and of 0.464, and blowing with argon rinsing, 0.474 and of 0.459.

## 5 CONCLUSIONS

1. On the basis of the thermodynamics, kinetics, mechanism and mass transfer conditions as well as the effect of slag addition it was concluded that it was possible to ensure the selective oxidation of manganese in hot metal without significantly affecting the content of the other elements.
2. Through the pilot-plant oxidation of only manganese at 1573 K it was possible to determine suitable values of the technological and metallurgical parameters to achieve an optimal decrease for the high initial manganese content in the hot metal.
3. Considering the influence of oxygen and $Fe_xO$ for the checked oxidation variants, it is obvious that the optimal mechanism of selective oxidation of the manganese is connected with the kinetics of the supply of oxygen. The decrease of the manganese content is only achieved if the selective oxidation occurs in three reaction fields.
4. During the oxidation of manganese, other elements are maintained at the initial contents or are minimally oxidised, as carbon, or silicon, depending on the $SiO_2$ in the slag.
5. The obtained results of the manganese oxidation do not lead to a secondary increase in the content of manganese in the hot metal.
6. From the environmental point of view, of all the checked variants, the variant 3 is the most acceptable, as in the processing no brown fumes are produced.

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