

# EXPERIMENTS ON THE DEPHOSPHORIZATION OF HIGHLY ALLIED MANGANESE STEEL WITH HIGH PHOSPHORUS

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## Abstract:

The practical application of dephosphorization is discussed in the paper. Using the method of austenitic manganese steel waste re-melting, we get inevitable, phosphorus contents that exceed the admissible limits. The phosphorus increases the hardness and tensile strength of steel and it seriously affects the ductility and resistance to shock or impact. Experiments on the dephosphorization of highly allied manganese steel containing high phosphorous was made in laboratory conditions and the experimental results showed that the content of phosphorous in the steel can be lowered quickly and considerably. The industrial conditions allowed us to obtain similar results with those obtained in the laboratory. The only difference between the two experiments is the dephosphorization level, which was higher in the laboratory compared to the level obtain on an industrial scale, even if the experiments were done in similar conditions.

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## 1. INTRODUCTION

Manganese steel (or Hadfield steel) is unique nonmagnetic steel with extreme anti wear properties [1-3,6,11-15]. Also, manganese steel was unique in that it combined high toughness and ductility with high work hardening capacity and, usually, good resistance to wear. Manganese steel is known for its high impact strength and resistance to abrasion [1-3,6,11-15]. Under shock and during conditions of impact it nearly triples its initial surface hardness and acquires a high polish, without any increase in brittleness which is usually associated with hardness.

Manganese steel is made by alloying steel, containing 0.8 to 1.25% carbon, with 11 to 15% manganese (an average of around 13% manganese) [1-3,6]. Many variations of the original austenitic manganese steel have been proposed, but only a few have been adopted as significant improvements. These usually involve variations of carbon and manganese, with or without additional alloys such as chromium, nickel, molybdenum,

vanadium, titanium, and bismuth. The mechanical properties of austenitic manganese steel vary with both carbon and manganese content [6,10-15]. As carbon is increased it becomes increasingly difficult to retain all of the carbon in solid solution, which may account for reductions in tensile strength and ductility. It is known the fact that the manganese steel hardness, after the thermal treatment, is situated between 180 and 220 HB, but, under the influence of the vibratory load and the high specific pressures, at the surface it is formed a significant number of slip planes and therefore, a consolidation and an increase of secondary hardness. This allows manganese steel to retain its toughness. These features, combined with the high tensile strength, make it an ideal material for heavy impact and abrasive service. Manganese steel performs best in extreme impact applications.

Manganese steel has been used in the mining industry, cement mixers, and rock crushers, crawler treads for tractors and other high impact and abrasive environments [1-3,6]. Giving the destination of these steel, it is very important that

the phosphorus content does not exceed the admissible limits (max. 0.11%). The phosphorus results in steel from the metallic charges which can be between 45-98% recycled wastes of manganese steel. Another source to introduce the phosphorus in the metallic bath is the ferro-manganese [1-9]. The phosphorus, in the manganese steel, can be found as solid solution inside the austenitic granule. When the phosphorus content increases over 0.12%, the free complex phosphide fixes at the austenitic granule margins, which causes fragility both at low and at high temperatures [1-9].

Using the method of austenitic manganese steel waste re-melting, we get inevitable, phosphorus contents that exceed the admissible limits [1-9, 17-18]. The phosphorus increases the hardness and tensile strength of steel and it seriously affects the ductility and resistance to shock or impact. For this reason, the functioning durability of the manganese steel cast pieces highly decreases and, in the same time, it increases the cull quantity, because of the defects like heat crack and cold crack [4,6,16,17].

The defects in the manganese steel cast pieces, with accent on the defects caused by the increased content of phosphorus, were analyzed in the foundry [3,4,6]. In this way, the heat cracks - caused by the high phosphorus content (Fig.1 and Fig.2), the cold cracks (Fig.3 and Fig.4) and the structural defects in the cast pieces from highly allied steel with manganese appeared (Fig.5-10).



**Fig.1.** Heat cracks (P = 0.139%), appeared during at the thermal treatment



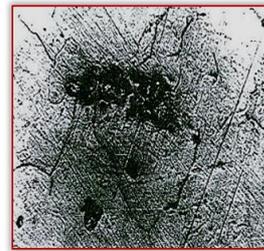
**Fig.2.** Heat cracks (P=0.134%), appeared during at the thermal treatment



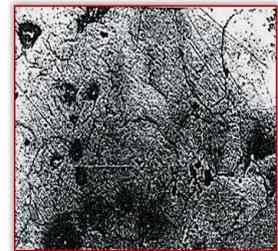
**Fig.3.** Cold cracks, appeared at gagging (P=0.136%)



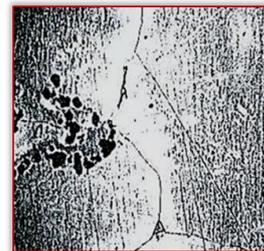
**Fig.4.** Cold cracks, appeared at gagging (P=0.139%)



**Fig.5.** Microcavities, microcracks and inclusions (case of P=0.126%) in the Austenitic structure (x500)



**Fig.6.** Microcracks, inclusions, un-dissolved white carbides (case of P=0.126%) in the Austenitic structure (x500)



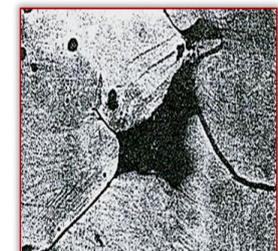
**Fig.7.** Microcavities, inclusions, un-dissolved white carbides and microcracks (case of P=0.129%) in the Austenitic structure (x500)



**Fig.8.** Inclusions, small un-dissolved white carbides and inter-crystalline microcracks (case of P=0.128%) in the Austenitic structure (x500)



**Fig. 9.** Inclusions, un-dissolved white carbides and microcracks (case of P=0.128%) in the Austenitic structure (x500)



**Fig. 10.** Micro cracks and un-dissolved white carbides (case of P=0.139%) in the Austenitic structure (x500)

## 2. LABORATORY EXPERIMENTS AND RESULTS

In the Metallurgy Laboratory, from the Faculty of Engineering – Hunedoara, a series of three tests were made, with the purpose of manganese steel dephosphorization. The samples, weighing 1 kg, were obtained from cast charges that had a high phosphorus content ( $P_{max}=0.11\%$ , according to the Romanian requirements, Table 1).

**Table 1.** Chemical composition of the samples

Samples no.	Carbon [%]	Manganese [%]	Silicon [%]	Phosphorus [%]
1	1.40	13.24	0.83	0.129
2	1.34	13.46	0.76	0.126
3	1.39	13.59	0.33	0.134

With the first sample, the dephosphorization with the slag elimination at melting is experimented. In the charge were introduced the following materials:

- > 1.8% iron ore (pellet),
- > 1.5% lime,
- > 1.0% calcium–fluorite,

which means a total of 4.3% addition. After melting, the entire slag was removed, and the liquid steel was cast in the chill mould. The chemical composition of the first sample is presented in Table 2.

**Table 2.** Chemical composition, after laboratory experiments

Samples no.	Manganese [%]	Silicon [%]	Phosphorus [%]
1	7.27	0.27	0.034
2	5.74	0.17	0.031
3	8.72	0.31	0.077

With the second sample, the quantity of addition on the charge was increased, as follows:

- > 3.0% CaO,
- > 1.0% CaF<sub>2</sub>,
- > 2.0% ACC scrap (autoclaved cellular concrete),
- > 2.0 % iron ore (pellet),

which means a total of 8.0% addition. After melting, the slag was removed, and the steel was cast in the chill mould. The chemical composition of the second sample is presented in the same Table 2.

With the third sample, a melting with two slags was attempted. In the charge were introduced the following addition materials:

- > 3.0% CaO,
- > 3.0% ACC scrap (autoclaved cellular concrete),
- > 2.0 % iron ore (pellet).

which means a total of 8% addition. After melting, the slag was removed and the following additions are introduced, in order to form the new slag:

- > 2.0% CaO,
- > 0.6% CaF<sub>2</sub>,
- > 0.4% ACC scrap (autoclaved cellular concrete),
- > 1.5% FeSi,
- > 0.5% Al.

This slag was not removed this time, and the chemical composition of the sample cast in the chill mould is presented in Table 2.

## 3. INDUSTRIAL EXPERIMENTATIONS AND RESULTS

At an industrial scale, with the same purpose as the laboratory experiments, a dephosphorization in the 3 tone capacity electrical furnace with basic lining has been attempted.

The chemical composition of the charge has been between the limits prescribed by the standards, except the phosphorus. The metallic charge was formed by:

- > 70% recycled waste (riser) of manganese steel, with high content of phosphorus, between 0.125–0.144%,
- > 30% acquired manganese steel waste.

We have been experimented the dephosphorization on three charges. With the first charge, on the load (approximately 3 tones), the following additions have been made:

- > 40 kg CaF<sub>2</sub>,
- > 60 kg iron ore (pellet),
- > 80 kg lime.

After melting, the composition of the metallic bath is presented in Table 3.

**Table 3.** Chemical composition of the charges, after the industrial experiments

Charges no.	Manganese [%]	Silicon [%]	Phosphorus [%]
1	8.11	0.19	0.086
2	8.79	0.24	0.091
3	8.94	0.22	0.093

In this phase, more additions were made on the metallic bath (consisting in 40 kg lime, 30 kg CaF<sub>2</sub> and 15 kg FeSi), after which the correction with FeMn was made, for maintaining the manganese content in the imposed limits.

With the second and third charge, the addition quantities are increased, as follows:

- > 45 kg CaF<sub>2</sub>,
- > 60 kg iron ore (pellet),
- > 90 kg lime.

After melting, the chemical compositions of the two charges are presented in Table 3. The melting slag has not been removed in either of the charges.

#### 4. CONCLUSIONS

After the laboratory and industrial experiments, the following conclusions can be made:

- analyzing the industrial data, one can notice that a manganese steel dephosphorization is possible;
- although the content of manganese is decreasing, at an advanced dephosphorization, the dephosphorated cast iron pieces present a superior resistance to wear compared to cast iron pieces through the remelting without dephosphorization method. In the same time, the quantity of waste is considerable reduced, because of the mentioned defects;
- based on the laboratory experiments (melting in the graphite crucible furnace), one can observe the possibility to perform the dephosphorization for highly allied steel with manganese;
- if the casting temperatures could have been measured, we consider that the results would have been even more conclusive.

Using the manganese steel waste remelting method, can inevitable obtain phosphorus quantities that exceed the maximum admissible limit. This is the reason that the functioning durability of the manganese steel casts is decreasing, but, in the same time the waste quantity is increasing considerably, caused by the defects like heat creaks and cold creaks.

The industrial conditions grant to obtain similar results with those obtained in the laboratory. The only difference between the two experiments is the dephosphorization level, which was higher in the laboratory compared to the level obtain on an industrial scale, even if the experiments were done in similar conditions. The motives for witch those differences appeared are:

- the casting temperature, in the laboratory experiments, could not been controlled;
- the laboratory conditions did not allow a rigorous control over the quantity and the chemical composition of the slag;
- on a industrial scale, recycled waste presented molding sand adhesion.

Analyzing the obtained data, one can notice that an industrial scale manganese steel dephosphorization is possible.

#### REFERENCES

- [1] V. Cojocaru-Filipiuc, Steel making and structural aspects of the ferrous alloys (obținerea oțelului și aspecte structurale ale aliajelor feroase), Samia Publishing House, Iași, 2005.
- [2] V. Geantă, R. Ștefănoiu, The steel making engineering (Ingineria producerii oțelului), BREN Publishing House, București, 2008.
- [3] I. Butnariu, V. Geanta, Advanced technologies for steel making and refining treatment (Tehnologii speciale de elaborare si rafinare a otelului), Universitatea Politehnica Publishing House, București, 1993.
- [4] O. Wijk, The phosphorus problem in iron and steel making, Scand. J. Metall., 22 (3), 1993: pp.130-138.
- [5] N. Masumitsu, K. Ito, R. J. Fruehan, Thermodynamics of Ca-CaF<sub>2</sub> and Ca-CaCl<sub>2</sub> systems for the dephosphorization of steel, Metall. Mater. Trans. B, 19 (4), 1988: pp.643-648.
- [6] I. Kiss, Industrial and laboratory experiments regarding the dephosphorization possibilities of highly allied steel with manganese, Annals of F.E.H. – Int. J. of Eng., 10 (3), 2012: pp.385-388.
- [7] P. N. Chaudhary, R. K. Minj, R. Krishna, R. P. Goel, Selective removal of phosphorus from high carbon ferromanganese - an improved process, Met. Mater. Process., 16 (2-3), 2004: pp.217-226.
- [8] T. Borovský, J. Kijac, M. Domovec, The slag composition influence on the dephosphorization and on the lifetime of electric arc furnace hearth refractory lining, Acta Metall. Slovaca, 16 (3), 2010: pp.165-171.
- [9] T. Borovský, J. Kijac, B. Bulko, M. Domovec, J. Havran, The effectiveness of dephosphorization with and without fluorspar using in the electric arc furnace steelmaking, Acta Metall. Slovaca, 17 (4), 2011: pp.263-268.
- [10] J. Adamczyk, A. Grajcar, Structure and mechanical properties of DP-type and TRIP-type sheets, J. Mater. Process. Technol., 162-168 (-), 2005: pp.267-274.
- [11] L.A. Dobrzanski, A. Grajcar, W. Borek, Microstructure evolution and phase composition of high-manganese austenitic

- steels, *Journal AMME*, 31 (2), 2008: pp.218-225.
- [12] L.A. Dobrzanski, A. Grajcar, W. Borek, Microstructure evolution of high-manganese steel during the thermos-mechanical processing, *Archives of Mat. Sc. and Eng.*, 37 (2), 2009: pp.69-76 .
- [13] L. A. Dobrzański, A. Grajcar, W. Borek, Influence of hot-working conditions on a structure of high-manganese austenitic steels, *Journal AMME*, 29 (2), 2008: pp.139-142.
- [14] L. A. Dobrzański, A. Grajcar, W. Borek, Hot-working behavior of high-manganese austenitic steels, *Journal AMME*, 31 (1), 2008: pp.7-14.
- [15] P. Rama Rao, V. V. Kutumbarao, Developments in austenitic steels containing manganese, *Int. Mater. Rev.*, 34 (1), 1989: pp.69-92.
- [16] V. Shankar, T. P. S. Gill, S. L. Mannan, S. Sundaresan, Solidification cracking in austenitic stainless steel welds, *Sadhana*, 28 (3-4), 2003:pp.359-382.
- [17] H. Erhart, M. Paju, Phosphorus segregation in austenite, *Scripta Metall. Mater*, 17 (2), 1983: pp.171-174.
- [18] A. Hernandez, A. Romero, F. Chavez, M. Angeles, R.D. Morales, Dephosphorization and desulfurization pretreatment of molten iron with CaO-SiO<sub>2</sub>-CaF<sub>2</sub>-FeO-Na<sub>2</sub>O slags, *ISIJ International*, 8 (2), 1998: pp.126-131.