PURITY REQUIREMENTS FOR Mn-ALLOYS FOR PRODUCING HIGH MANGANESE TRIP AND TWIP STEELS

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ABSTRACT

Manganese is the main alloying element used in the production of high manganese TRansformation-Induced Plasticity (TRIP) and TWinning-Induced Plasticity (TWIP) steels. These types of steels require low concentrations of the impurities such as P, N, C to show their unique properties. Since manganese is introduced to these steels through the application of manganese alloys, the impurity concentrations in the manganese alloys have to be at acceptable levels. In the present study, the purity requirements for ferromanganese and silicomanganese alloys for making TRIP and TWIP steels are studied. It is indicated that the levels of C, P and N in these ferroalloys are relatively high. The removal of these impurities in manganese alloys production and refining involves specific challenges to be responded. The alternative processes for removing these impurities are evaluated and it is shown that impurities removal requires the improvement of the charge materials for the Mn alloys production, or developing new refining processes.

KEYWORDS: *Manganese, TRIP, TWIP, steel, carbon, phosphorus, nitrogen.*

1. INTRODUCTION

Manganese (Mn) is the 12th abundant element in the earth's crust and it is ranked as the 4th most used metal in terms of tonnage behind Fe, Al, and Cu. More than 90% of the manganese produced around the world is used in steelmaking as a deoxidizer and sulphide former (30%) or as an alloying element (70%). According to the World Steel Association, 1.49 billion ton crude steel was produced in 2011 [1]. The world manganese alloys production in this year has been close to 16 million ton [2]. The share of different manganese alloys is shown in figure 1 and as we see high carbon ferromanganese (HCFeMn) is ranked first.

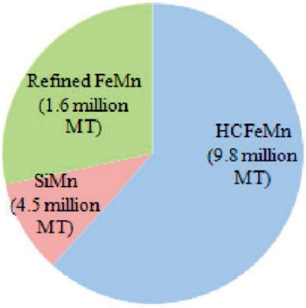


Figure 1: Global share of Mn alloys in 2011, data from ref [2]

The manganese content of steel grades varies with regard to the expected properties. Low carbon steels contain 0.15%-0.8% Mn, stainless steels contain mostly about 1% Mn. Hadfield steel, which is the first alloy steel ever invented contains 13% Mn or more. The Mn concentration in High

Strength Steels (HSS) such as Mild Steels, Interstitial Free (IF), Baked Hardenable (BH), High Strength Low Alloy (HSLA), and Solid solution-strengthened steels is mostly above 1%. The first generation of the Advanced High Strength Steels (AHSS); Dual Phase (DP), Complex Phase (CP), Martensitic (MART), and Transformation-Induced Plasticity (TRIP) steels were introduced in the late 1990's through the early 2000's. In these steel grades high amounts of bainite and martensite are used together with the conventional strengthening mechanisms to improve both the strength, formability, and energy absorption. The second generation of the AHSS is Light-weight steels with Induced Plasticity (L-IP), Shear band Induced Plasticity (SIP) and Twinning-Induced Plasticity (TWIP) steels [3]. These steels offer excellent combinations of strength and ductility due to a largely FCC austenite base structure, compared to the largely ferrite base structure in the first generation AHSS. Figure 2 shows the strength-ductility regime of high strength steels and as we see high manganese TRIP and TWIP steels show both high tensile strength and elongation compared to the other high strength steels [4]. A high manganese TRIP steel resist high stresses without deforming. TWIP steel deforms with low stresses and does not break until high strain is reached i.e. around 90% [4, 5].

With regard to the excellent mechanical properties of high Mn TRIP and TWIP steels, their commercialization is expected for many applications. In particular, for the automotive industry they cause light-weighting of the car, whereas the increase of ductility allows for more complex car design [6]. Application of these steels improves the fuel economy and decreases the greenhouse gas emissions, while they improve the safety [7, 8]. Since the high manganese content of these steels is mainly added in the steelmaking, the utilized manganese alloys should not introduce harmful impurities to the steel. Moreover, the manganese alloys should not affect the steelmaking process regarding the removal of the unwanted impurities. In the present work, the chemical requirements for manganese alloys for producing high Mn TRIP and TWIP steels are studied.

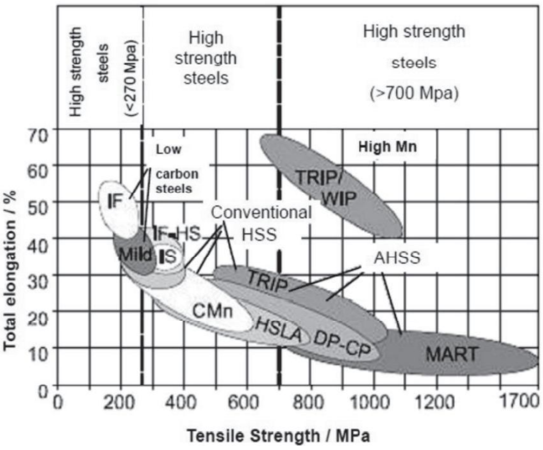


Figure 2: The strength-ductility regime of high strength steels [4]

2. ELEMENTS IN HIGH MN TRIP AND TWIP STEELS

Depending on Mn and C levels in the steels different microstructures can be obtained. For instance, in ferrite-martensite DP steels, ferrite and martensite phases co-exist in the alloy. Whereas, for low Mn TRIP steels bainite and retained austenite exist in addition. The dispersion of these hard secondary phases in the soft ferrite creates a high work hardening rate, and in TRIP steels the retained austenite is transformed to ε-martensite with increasing strain. With increasing the share of Mn, Si and Al in the iron crystal, the TRIP effect is increased and the steel shows higher ductility. This is due to the effect of these elements in multiple martensitic transformations [5]. According to

Formmeyer et al. [5], the TRIP effect occurs if the changes in the Gibbs free energy of phase transformation from austenite to ε-martensite is less than -220 J/mol and the stacking fault energy is less than 16 mJ/m^2. If the changes of the Gibbs free energy of phase transformation from austenite to ε-martensite are between 110 and 250 J/mol, and the stacking fault energy is less than 25 mJ/m^2, extensive twin formation occurs under mechanical effect, which is known as Twining-Induced Plasticity (TWIP) effect.

High Mn TRIP and TWIP steels contain high concentrations of Mn and higher Si and Al concentrations than many steel grades. Table 1 shows typical collected available chemical composition data for these kinds of steels. It is observed that they contain high Mn concentrations in the ranges between 15 and 30 wt%. The role of Mn in these steels is austenite stabilizer. These high Mn levels have not ever been in any commercialized steel product in mass production. Table 1 shows Si and Al concentrations between 2 and 4 wt%. The high Al content increases the stacking fault energy of austenite and it suppresses the formation of martensite. It also improves the low temperature toughness of the steel [4]. Silicon improves strength by solid solution strengthening and it is effective for refining martensite plates and increasing fracture strength, although it does not improve the ductility [4].

Table 1: Chemical compositions of typical high Mn TRIP and TWIP steels

Reference	Mn,wt%	S , wt%	Al, wt%	C, ppmw	N, ppmw	P, ppmw	S, ppmw
Grassel et al. (2000)	15.9-16.2	1.9-4.0	1.8-3.5	100-200	N.A.	N.A.	N.A.
Grassel et al. (2000)	18.1-20.1	1.8-4.3	1.8-3.5	300-600	N.A.	N.A.	N.A.
Grassel et al. (2000)	25.5-26.5	2.0-3.9	1.8-3.8	300	N.A.	N.A.	N.A.
Grassel et al. (2000)	28.7-30.6	2.0-4.0	2.0-3.9	100-200	N.A.	N.A.	N.A.
Frommeyer et al. (2003)	15.8	3.0	2.9	200	<30	N.A.	N.A.
Frommeyer et al. (2003)	20.1	2.8	2.9	400	<30	N.A.	N.A.
Frommeyer et al. (2003)	25.6	3.0	2.8	300	<30	N.A.	N.A.
Vercammen et al. (2004)	29.4	3.0	3.3	N.A.	N.A.	N.A.	33

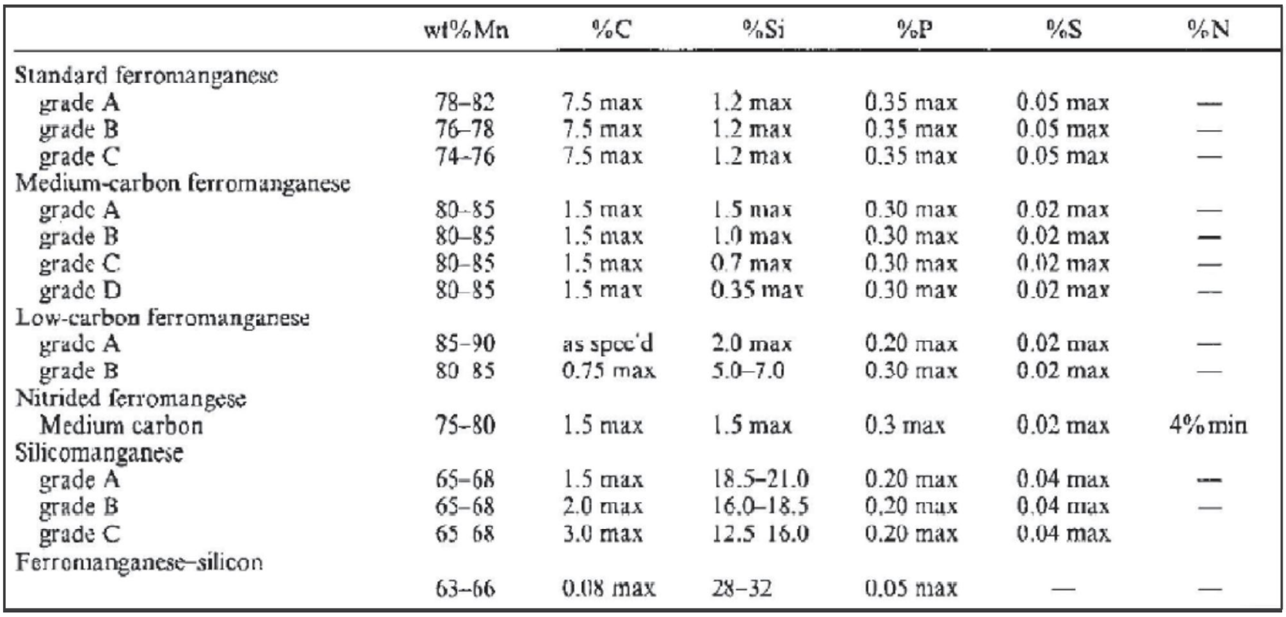
The chemical data in table 1 indicates that high Mn TRIP and TWIP steels contain relatively low carbon concentrations and roughly below 500 ppm. Carbon is austenite stabilizer and it strengthens austenite by solid solution hardening mechanism. Carbon inhibits the formation of martensite by increasing the stacking fault energy. It has been suggested that only the retained austenite with optimum carbon content can provide the TRIP/TWIP effect and improve the elongation [9]. There are also typical studies on using relatively high carbon concentrations i. e. 0.2 wt% [10, 11]. According to Cooman et al. [12], however, high Mn TWIP steels containing 200-6000 ppm carbon have reached the stage of large scale industrial testing with industrial focus on TWIP steels production. In general, the strength of TWIP steels is increased with increasing the carbon concentration[13], and since the formability of the steel is necessary for the product forming, we may say that low carbon TWIP steels are more favorable.

Nitrogen plays the same role as carbon and its concentration is low and below 30 ppm as seen in table 1. It has been observed that both strength and elongation are improved with increasing the N concentration of the low Mn TRIP steels from 30 ppm to 100 ppm [14]. However, its effect on high Mn TRIP and TWIP steels is not clear yet. No information about the optimal concentrations of P and S in these steel grades has been reported. We may consider having levels below 100 ppm and 50 ppm for P and S, respectively, as many other steel grades.

3. USING MN ALLOYS FOR MAKING TRIP AND TWIP STEELS

In order to make High Mn TRIP and TWIP steels with the mentioned maximum acceptable levels of C, N, P and S, the chemical composition of Mn alloys should be in acceptable levels. The chemical compositions of the Mn alloys from different references are shown in tables 2 and 3. These data and their comparison with the chemical compositions of the High Mn TRIP and TWIP steels (table 1) may indicate that the application of low carbon Mn alloys is the most reasonable way to maintain the required low C concentrations in the steels. It is worth mentioning that the decarburization of molten steel is accompanied with significant amount of Mn and Si losses and it is not feasible after the addition of ferromanganese and silicomanganese to the molten steel.

Table 2: ASTM standard specification for manganese ferroalloys (1999)



	wt%Mn	%C	%Si	%P	%S	%N
Standard ferromanganese						
grade A	78–82	7.5 max	1.2 max	0.35 max	0.05 max	—
grade B	76–78	7.5 max	1.2 max	0.35 max	0.05 max	—
grade C	74–76	7.5 max	1.2 max	0.35 max	0.05 max	—
Medium-carbon ferromanganese						
grade A	80–85	1.5 max	1.5 max	0.30 max	0.02 max	—
grade B	80–85	1.5 max	1.0 max	0.30 max	0.02 max	—
grade C	80–85	1.5 max	0.7 max	0.30 max	0.02 max	—
grade D	80–85	1.5 max	0.35 max	0.30 max	0.02 max	—
Low-carbon ferromanganese						
grade A	85–90	as spec'd	2.0 max	0.20 max	0.02 max	—
grade B	80 85	0.75 max	5.0–7.0	0.30 max	0.02 max	—
Nitrided ferromangese						
Medium carbon	75–80	1.5 max	1.5 max	0.3 max	0.02 max	4% min
Silicomanganese						
grade A	65–68	1.5 max	18.5–21.0	0.20 max	0.04 max	—
grade B	65–68	2.0 max	16.0–18.5	0.20 max	0.04 max	—
grade C	65 68	3.0 max	12.5 16.0	0.20 max	0.04 max	
Ferromanganese–silicon						
	63–66	0.08 max	28–32	0.05 max	—	—

Table 3: Typical chemical compositions of Mn ferroalloys

Reference	Mn, wt%	Fe, wt%	Si, wt%	C, wt%	P, wt%	N, pmw	S, ppmw
HC FeMn (Hoel, 1998)	79	13.5	0.2	7.0	0.18	300	20
MC FeMn (Hoel, 1998)	81	16.5	0.5	1.5	0.17	1200	40
LC FeMn (Hoel, 1998)	82	17	0.3	0.5	0.18	1200	30
VLC FeMn (Hoel, 1998)	80	19	0.3	0.2	0.18	1300	-
MC SiMn (Hoel, 1998)	69	10	19	1.5	0.08	50	90
LC SiMn (Hoel, 1998)	61	9.5	29	0.1	0.05	-	30
Std. SiMn [producer]	-	-	-	-	0.1	140	170
LC SiMn [producer]	-	-	-	-	0.05	30	80

Considering the carbon level as a limitation in Mn ferroalloys selection for making high Mn TRIP/TWIP steels, the feasibility of using low carbon alloys can be studied. An ideal case study may be using VLC FeMn and LC SiMn alloys (table 3) for production of 100 kg of typical steels such as Fe-15Mn-3Si-3Al, Fe-20Mn-3Si-3Al, Fe-25Mn-3Si-3Al. Table 4 shows the required amounts of the alloys VLC FeMn and LC SiMN to make the above mentioned steel qualities. The calculations are simple mass balances and include the introduced amounts of the main trace elements (C, P, N and S). It is worth mentioning that the S concentration for the VLC FeMn was considered as 20 ppm, which is fairly acceptable with regard to the analysis of the other types of FeMn. The calculations are based on alloying molten steel containing 0.01 wt% C, 30 ppm P, 30 ppm N and 30 ppm S, which is reasonable considering well decarburized steel. Decarburization to such low levels is generally considered costly in steelmaking.

Table 4: Required Mn alloys for producing high Mn TRIP/TWIP steels, and typical impurity levels in the alloyed steels

High Mn steel analysis	**Required masses of Mn alloys for 100 kg steel, kg**		**Impurity levels in the steel product after alloying, ppmw**			
	VLC FeMn	**LC SiMn**	**C**	**P**	**N**	**S**
15Mn-3Si-3Al	10.8	10.3	475	293	187	51
20Mn-3Si-3Al	17.1	10.3	587	402	265	49
25Mn-3Si-3Al	23.4	10.3	700	511	342	47
Assumed max leveles tolerated	-	-	500	100	100	50

*This concentration is here proposed as optimal with regard to usual steel grades.

The data in table 4 and the above discussion on the compositions of high Mn TRIP and TWIP steels may indicate that the S content of the manganese ferroalloys is relatively low and almost acceptable. The carbon content of VLC FeMn and LC SiMn is acceptable or not with regard to the expected carbon content in the final steel product. The concentrations of both P and N in VLC FeMn and LC SiMn are high for steelmaking. Hence, the removal of C, P and N from manganese ferroalloys may be necessary. The feasibility of the elimination of these three impurities in the Mn alloys production processes are studied as follows.

4. ULTRA LOW CARBON MN ALLOYS PRODUCTION

The carbon content of FeMn and SiMn can be decreased to acceptable levels for specific grades of high Mn TRIP and TWIP steels. The decarburization of FeMn is mainly performed in oxygen refining process [15, 16] in which the dissolved carbon in FeMn is oxidized by oxygen blowing. VLC FeMn can be produced in this process and it might be possible to further decrease the carbon level. According to Lee and Kolbeinsen [16], the rate of the decarburization of FeMn in low carbon concentrations is controlled mainly by the mass transport of the dissolved carbon in the melt. Therefore, the main challenge in ultra-low carbon FeMn (ULC FeMn) production will be the significant amount of Mn loss for decreasing a small amount of the carbon in low concentrations. This may cause relatively higher product costs for ULC FeMn. Hence, developing alternative cost effective refining processes for producing ULC FeMn is important.

The decarburization of SiMn is usually done through the introduction of FeSi to silicomanganese in ladle refining process [15]. In general, the carbon content of the SiMn alloys is decreased with increasing the Si content. For instance, the equilibrium dissolved carbon in Mn-Fe-Si alloy with Mn/Fe=5 with 25 %Si at 1500 ºC is around 0.38wt%, whereas it is around 0.05wt%

for the same alloy containing 35%Si [17]. In principle, the production of ultra low carbon SiMn (ULC SiMn) is feasible with this process and from practical point of view it is more promising than producing ULC FeMn.

5. LOW PHOSPHORUS MN ALLOYS PRODUCTION

Phosphorus in manganese alloys originates from the charge materials of the furnace and mainly the manganese ore regarding its tonnage. Phosphorus content of industrial manganese ores can be typically 0.03wt% to 0.11wt% [18]. The metallurgical coke that is mostly used as the reductant contains also phosphorus, typically 0.14wt% and 0.5wt% [19]. The input phosphorus to the furnace goes mainly to the alloy product; while the manganese content of the slag is negligible. In general, the P concentration in SiMn is less than FeMn due to the existence of P in the Mn ore. The application of FeMn slag which contains very low P in SiMn furnace as the Mn source causes less P input to the furnace and consequently lowers P in the SiMn product. The removal of P from the Mn alloys requires using low P charge materials or the development of dephosphorization refining processes for the alloys.

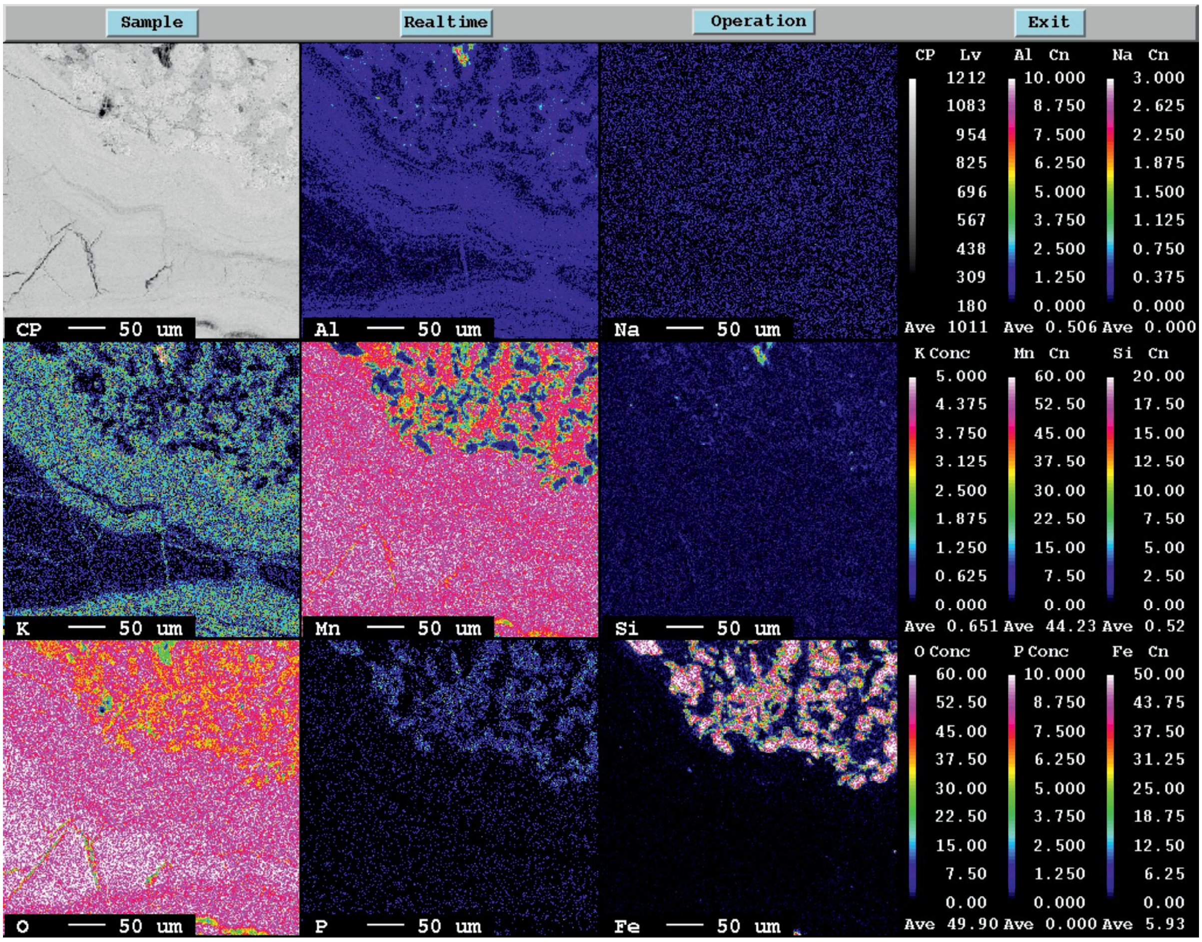
Regarding the fact that P is mainly originated from the manganese ore, an alternative process for low phosphorus FeMn (LPFeMn) production is using low P manganese ores or dressed ores. However, P is always present in Mn ore and it is intimately associated with Fe and Mn in the ore as shown for a typical ore in figure 3. This means that the application of ore dressing techniques for dephosphorization of Mn ore is not much beneficial. Moreover, ore dressing causes the Mn concentrate production and therefore particular agglomeration techniques i.e. pelletizing is required to produce suitable furnace charge material. These processes will increase the costs of the raw materials and in turn the costs of Mn alloys products. Thus, Mn ore dressing with the aim of P elimination cannot be feasible as long as acceptable grades of Mn ores are available and ore dressing for increasing the Mn content is not required.

Refining of the produced Mn alloys is another alternative for producing LPFeMn. Gaseous dephosphorization and vacuum refining techniques may not be acceptable with regard to the high vapor pressure of Mn and significantly high amounts of Mn loss. The phosphide product in such processes produces toxic phosphine in exposure to moisture and it needs safety precautions. Oxidative refining by BaO based fluxes is another alternative, in which P is removed through the following reaction:

$$3/2\ \mathrm{BaO}\ (s) + [\mathrm{P}] + 5/2\ \mathrm{MnO}(l) = 5/2\ \mathrm{Mn}\ (l) + \mathrm{Ba}_{3/2}\mathrm{PO}_4\ (s)$$

Dashevskii et al. [20] treated HCFeMn by BaO containing slags and they observed better P removal with increasing BaO and CaO in the slags. This technique may be suitable for P elimination from FeMn alloys. However, the challenge will be provision of barium oxide flux containing low P at a reasonable price.

It was mentioned above that SiMn contains low P when the Mn source is the slag from FeMn furnace. The application of a process in which HCFeMn slag is used to produce LPFeMn is an alternative process as shown in figure 4 is proposed. In this process the input P to the HCFeMn furnace is mostly distributed in the alloy product and the slag with low P content and relatively high MnO concentration i.e. 40 wt% is further reduced to produce LP HCFeMn. Further oxidative refining of this alloy for decarburization will also increase the P removal.



CP Lv	Al Cn	Na Cn
1212	10.000	3.000
1083	8.750	2.625
954	7.500	2.250
825	6.250	1.875
696	5.000	1.500
567	3.750	1.125
438	2.500	0.750
309	1.250	0.375
180	0.000	0.000
Ave 1011	Ave 0.506	Ave 0.000

K Conc	Mn Cn	Si Cn
5.000	60.00	20.00
4.375	52.50	17.50
3.750	45.00	15.00
3.125	37.50	12.50
2.500	30.00	10.00
1.875	22.50	7.50
1.250	15.00	5.00
0.625	7.50	2.50
0.000	0.00	0.00
Ave 0.651	Ave 44.23	Ave 0.52

O Conc	P Conc	Fe Cn
60.00	10.000	50.00
52.50	8.750	43.75
45.00	7.500	37.50
37.50	6.250	31.25
30.00	5.000	25.00
22.50	3.750	18.75
15.00	2.500	12.50
7.50	1.250	6.25
0.00	0.000	0.00
Ave 49.90	Ave 0.000	Ave 5.93

Figure 3: X-ray map of the distribution of elements in a commercial Mn Ore [18]

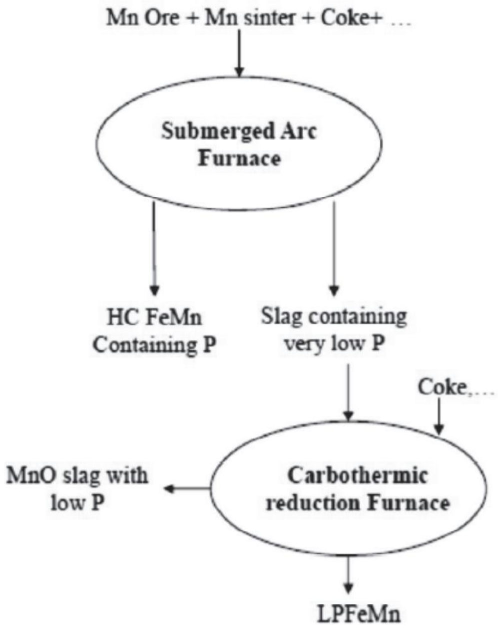


Figure 4: Alternative LP FeMn production process from HC FeMn slag

6. NITROGEN REMOVAL FROM MN ALLOYS

Nitrogen enters to the molten Mn alloys in exposure to air and through the oxidative decarburization process. This can be easily seen through comparing its concentration in HC FeMn with the other types of FeMn (table 3). Therefore, the amount of this impurity can be decreased through using nitrogen free gases in decarburization process and preventing the melt contact with the air. Another alternative might be using the well-known degassing techniques for the molten metals such as stream degassing and ladle degassing. However, such processes may cause significant Mn loss and dust production. Another alternative can be N removal through its entrapping to a slag phase. All potential refining processes for N elimination from Mn alloys affect the final product cost.

7. SUMMARY

High Mn TRIP and TWIP steels show excellent properties compared to the other high strength steels and this may cause their massive production in future. For making these steels FeMn and SiMn alloys containing very low levels of carbon, phosphorus and nitrogen may bedemanded. The production of these high purity Mn alloys requires development of new decarburization processes or optimization of the exisisting technologies for further carbon removal. Similarly, the nitrogen elimination requires development or application of new refining techniques. The production of low phosphorus Mn alloys requires specific considerations on the use of low phosphorus charge materials into the electric furnace, or the development of the new processes dedicated to P removal from the Mn alloys.

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