IMPURITIES IN COMMERCIAL FERROALLOYS AND ITS INFLUENCE ON THE STEEL CLEANLINESS

M. M. Pande[1i], M. Guo[1], X. Guo[1], D. Geysen[1], S. Devisscher[2], B. Blanpain[1], P Wollants[1]

[1] Dept. of Metallurgy and Materials Engineering, Katholieke Universiteit Leuven, Belgium
[2] ArcelorMittal Gent (Sidmar), Belgium

ABSTRACT

Ferroalloys are added during secondary steelmaking to impart special properties to the steel. Depending upon the ferroalloy quality this may lead to the formation of inclusions. The present knowledge lacks in the exact content of the individual elements and the nature of inclusions dispersed in the ferroalloys. In order to broaden the knowledge concerning ferroalloys' quality, five different ferroalloy grades (i.e. FeMo, FeNb, FeTi70, FeTi35 and FeP) were characterised for the impurity content. The ferroalloy samples were investigated for chemical analysis (ICP-AES and LECO combustion technique) and microstructural analysis (SEM-EDS). These impurities are linked to the ferroalloy manufacturing route. The inclusions observed in the microstructure are in good agreement with the inclusions extracted by the dissolution technique. In the present manuscript, the possible influence of ferroalloy quality over steel cleanliness is evaluated in the context of the impurities extracted and observed in the ferroalloys

1 INTRODUCTION

Ladle metallurgy or secondary refining serves an important purpose, where one of the main objectives is control of the number, shape, composition, morphology and size distribution of inclusions[1]. The cleanliness of steel[2-3] largely depends upon the secondary refining processes as it precedes the solidification of steel, apparently the last step during the manufacturing process as shown in **Figure 1**. One of the important steps in secondary metallurgy is the introduction of ferroalloys to steel.

Ferroalloys impart distinct properties to the steel. However, depending upon the purity of ferroalloys, there can be inadvertent entry of deleterious impurities (e.g. non-metallic inclusions) to the liquid steel. As a consequence of increased demands on steel properties, the effect of impurities in ferroalloys on the steel cleanliness has been a subject of special attention[4-7].

However, very little information is available in literature concerning the effect of ferroalloy impurities on steel quality with notable exceptions of Fe-Si[4], Fe-Mn[5-6]and Fe-Cr[7]. In FeMn, mainly oxides and oxysulphides inclusions were found. The nature and amount of inclusions found in Fe-Cr and Fe-Mn were found to be dependent upon the carbon content. Controlled alloying experiments[4,6,7] have been carried out by researchers for these ferroalloys. It was concluded that high purity Fe-Si additions resulted in higher steel cleanliness. However, the inclusions in FeCr were not inherited to the liquid steel in laboratory based experiments. The literature concerning the influence of other ferroalloys on steel cleanliness is very scarce.

In the present scenario, the ferroalloy manufacturer provides only partial information about the composition of the ferroalloys. Therefore, the present knowledge lacks in the exact content of the individual elements and the way impurities present in ferroalloys. In order to broaden the knowledge concerning ferroalloys' quality, five different ferroalloy grades were chosen for the impurities assessment. The impurities measured and observed for these ferroalloys are correlated with their manufacturing routes. Ferroalloy manufacturing routes are quite extensively described in the handbook of extractive metallurgy[9]. Based on the analysis results, influence of ferroalloy quality over the steel cleanliness is evaluated.

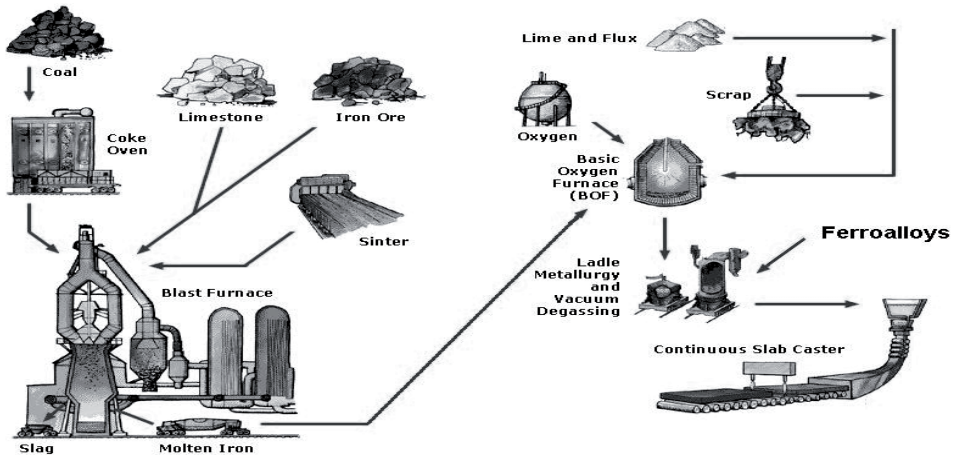


Figure 1: Overview of steelmaking showing various additions at different stages of the process [8].

2 INVESTIGATION METHODOLOGY

In all, five different ferroalloy grades were investigated, viz.: ferromolybdenum (FeMo), ferroniobium (FeNb), ferrotitanium (FeTi70 and FeTi35) and ferrophosphorus (FeP). These ferroalloys were commercially obtained.
The diagrammatic representation of the various techniques used for the detailed investigation of ferroalloys is shown in **Fig. 2**, which consists of sampling, compositional analysis and microstructural assessment of the ferroalloys.

2.1 Sampling

Three samples from each ferroalloy grade were randomly chosen for the analysis. One piece (25-30mm size) from each ferroalloy grade sample was manually crushed and randomly divided into three parts. One part with sufficiently coarse particles was prepared for micro-structural and phase identification. Two other parts were used for determining the alloy compositions.

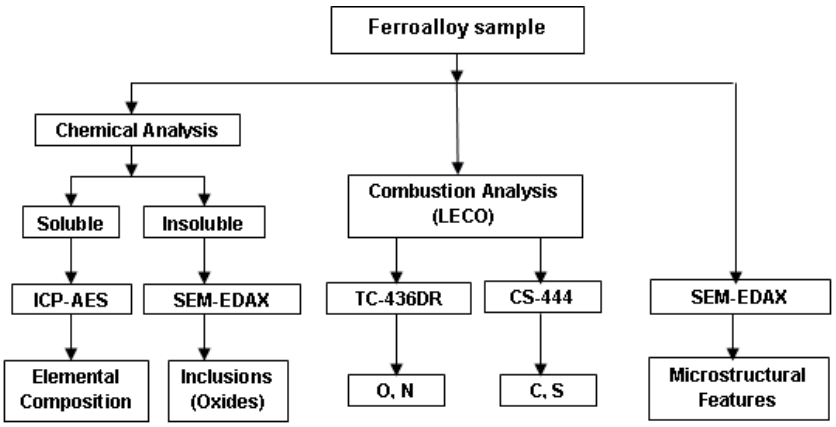


Figure 2: Methodology used for the investigation of ferroalloys

2.2 Compositional Analysis

One gram of ferroalloy powder was dissolved in different solvents. The combination of acids and their relative proportion used for dissolution of each ferroalloy grade is given in **Table 1**. The solutions obtained after the filtration with a 0.2 µm membrane were diluted thrice. The individual elements from various ferroalloy grades dissolved in the acids were analyzed with inductively coupled plasma atomic emission spectroscopy (ICP-AES, Varian Liberty series II instrument with an axial plasma configuration). The standards for analyzing ten different elements were prepared with the same acid concentrations as those of the sample solutions in six varying contents.

The acid insoluble (residue) fraction recovered on a filtration membrane was subjected to the assessments of size, shape and composition. This technique is based on the standard test method for acid-insoluble content of copper and iron powders ASTM: E 194-90[10].

Table 1: Acids used for the dissolution of ferroalloys

Ferroalloy grade	Solvents
FeMo	HCl + HNO_3 (3:1)
FeNb	HF + HNO_3 (1:3)
FeTi70	HCl
FeTi35	HCl
FeP	HCl + HNO_3 (3:1)

Nitrogen and oxygen contents in the ferroalloy samples were measured with a LECO combustion analyzer (TC-436DR). The accuracy level for oxygen and nitrogen measurement was, respectively, ±10 ppm and ±1 ppm. TC-436DR measures nitrogen by thermal conductivity and oxygen by infrared absorption. Carbon and sulphur contents of ferroalloy samples were measured with a CS-444 instrument. The CS-444 measures carbon and sulphur by infrared absorption. The accuracy levels for carbon and sulphur were ±4 ppm and ±2 ppm respectively.

2.3 Microstructural Investigation and Characterisation

Microstructural analysis and characterisation were carried out to know how the impurities are bonded in the ferroalloys as well as to assess size, shape and composition of the extracted inclusions (acid insoluble compound). These analyses were conducted by using a high resolution Philips XL30 FEG microscope equipped with an energy dispersive spectroscopy (EDS). The filtration membrane with the extracted inclusions on it was coated with carbon and then subjected to the characterisation. In order to investigate microstructure of the ferroalloys and identify the ferroalloy phases and the bonded impurities, the ferroalloy samples were impregnated in resin (Epofix) and polished with diamond suspensions. Finally, carbon was evaporated on the surface of the ferroalloy sample to provide a conducting layer.

3 RESULTS

3.1 Ferroalloy Composition and Impurities

The elemental composition obtained by ICP-AES is given in **Table 2**. As indicated by bold in the tables, the composition of each ferroalloy grade is an average of three samples. Different ferroalloys have different impurities depending upon their raw material used for the manufacture and the processing route. Among the ferroalloys under investigation, the individual impurity element does not exceed more than 1 wt% with the exception of Mn (2.3 wt%) and Ti (1.97 wt%) in FeP, Al (2.48 wt%) and V (1.83 wt%) in FeTi70, and Al (5.05 wt%) in FeTi35. The latter elemental impurities can lead to compositional fluctuation and complex reaction during alloying, thus bringing about problems in the steel cleanliness. There are certain elements like Ca[11-12] and Mg[13-14] which can affect the quality of steel even in minor quantities.

In addition to these elements, oxygen and sulphur in minor quantities can also impair the quality of steel. **Table 3** shows the results of LECO combustion analysis with total O, N, S and C contents of each ferroalloy grades. Most of the ferroalloy grades contain very limited nitrogen (around 50 ppm). Therefore, N pick up through these ferroalloy additions can be ignored for the secondary refining process. Carbon varies from 100 to 1200 ppm for the ferroalloy grades. Depending on the ferroalloy type and addition quantity, carbon pick-up in the steel has to be considered during alloying, specifically for the extra-low carbon steel production. Total O changes from 350 to 6500 ppm approximately with ferroalloy grade in an increasing order: FeNb (354 ppm) < FeP (1390 ppm) < FeTi70 (1859 ppm) < FeMo (6047 ppm) < FeTi35 (6476 ppm). Such a high oxygen level in the ferroalloys can inevitably affect steel cleanliness. Further discussions on the influence will be followed in more details in the section 4.2. On the other hand, around 200 ppm S was observed for the most of the ferroalloy grades except FeMo. It is necessary to take the sulphur impurity of the ferroalloy into account for the steel grades with extra-low sulphur content (e.g S < 5 ppm).

Table 2: Elemental composition in wt% of the ferroalloy grades analyzed by ICP-AES

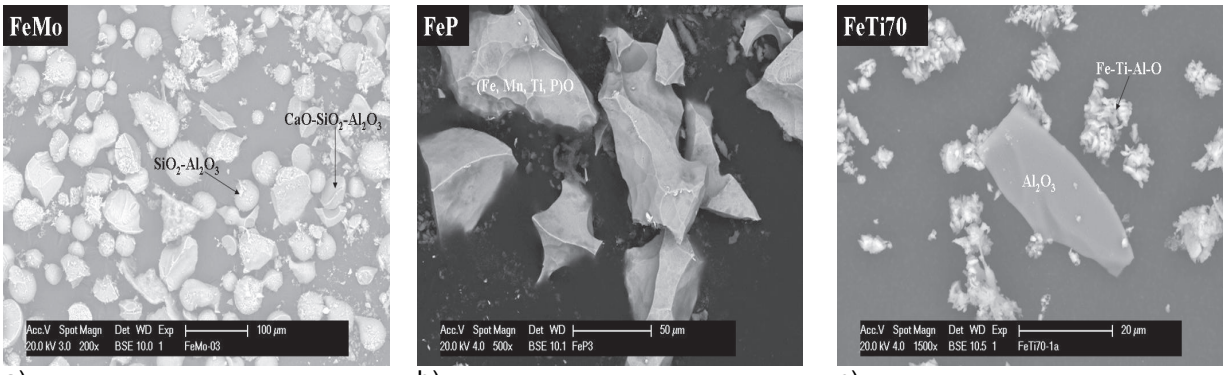
Sample No.	Ferro-alloy	Al	Ca	Fe	Mg	Mn	Mo	Nb	P	Ti	V
1-1	FeMo	0.88	-	24.85	-	-	73.39	-	-	-	-
1-2		0.81	-	31.42	-	-	67.24	-	-	-	-
1-3		0.85	-	27.68	-	-	70.46	-	-	-	-
Average		**0.85**	**-**	**27.98**	**-**	**-**	**70.36**	**-**	**-**	**-**	**-**
2-1	FeNb	0.99	-	30.61	0.75	0.23	1.41	65.38	-	0.37	-
2-2		0.97	-	28.94	0.66	0.23	1.36	67.06	-	0.51	-
2-3		0.86	-	31.09	0.65	0.24	1.41	65.09	-	0.40	-
Average		**0.94**	**-**	**30.21**	**0.69**	**0.23**	**1.39**	**65.84**	**-**	**0.43**	**-**
3-1	FeTi70	2.54	-	19.95	-	0.16	-	0.57	-	73.76	2.39
3-2		2.30	-	29.92	-	0.37	0.22	0.08	-	66.35	0.46
3-3		2.60	-	24.97	-	0.22	0.10	0.42	-	68.76	2.65
Average		**2.48**	**-**	**24.95**	**-**	**0.25**	**0.13**	**0.36**	**-**	**69.62**	**1.83**
4-1	FeTi35	4.52	0.19	45.87	-	0.55	-	0.16	-	47.41	0.50
4-2		4.71	0.24	47.68	-	0.56	-	0.17	-	45.09	0.37
4-3		5.93	0.23	58.12	-	0.77	-	0.14	-	34.02	0.39
Average		**5.05**	**0.22**	**50.56**	**-**	**0.63**	**-**	**0.16**	**-**	**42.17**	**0.42**
5-1	FeP	-	0.24	64.37	-	2.22	-	-	29.65	3.05	0.26
5-2		-	0.01	66.46	-	0.75	-	-	32.19	0.07	0.18
5-3		-	0.17	60.01	-	3.13	-	-	33.48	2.80	0.19
Average		**-**	**0.14**	**63.61**	**-**	**2.03**	**-**	**-**	**31.77**	**1.97**	**0.21**

Table 3: Composition of interstitial elements in parts per million analyzed by Leco combustion technique

Sample No.	Ferroalloy	O	N	C	S
1-1	FeMo	6558	126	1003	591
1-2		3034	27	759	745
1-3		8550	35	284	503
Average		**6047**	**63**	**681**	**614**
2-1	FeNb	397	-	431	104
2-2		336	14	618	105
2-3		329	40	475	109
Average		**354**	**18**	**508**	**106**
3-1	FeTi70	3512	14	1387	81
3-2		1059	39	802	47
3-3		1007	7	1348	47
Average		**1859**	**20**	**1179**	**65**
4-1	FeTi35	6112	4	698	98
4-2		9149	3	1327	127
4-3		4166	0	511	437
Average		**6476**	**2**	**845**	**221**
Average		**360**	**89**	**6573**	**164**
5-1	FeP	900	8	95	98
5-2		2252	10	141	112
5-3		1026	12	148	23
Average		**1390**	**10**	**128**	**78**

3.2 Extracted Inclusions from Ferroalloys

The acid insoluble residues or inclusions were extracted from the ferroalloys by the standard method[10] to analyze the size, shape and composition of the impurities present in the ferroalloys. This technique of inclusion extraction is not suitable for impurities like manganese oxide, calcium aluminate and sulphide inclusions. The use of strong acids like hydrofluoric acid (HF) for the dissolution of ferroniobium did not leave any residue after the dissolution. **Table 4** summarises the extraction results. It shows: (1) less than 0.5 wt% insoluble residues were extracted for FeP grade, 0.5-1.5 wt% for FeMo and FeTi70 grades and 9-9.5 wt% for FeTi35 grade. The insoluble impurities in FeMo grades mainly consisted of SiO_2 and Al_2O_3 (**Table 4**). In FeTi70, the insoluble impurities mainly consisted of Al-Ti-O inclusions and some particles of Fe-Al-Ti-O but in FeTi35, mostly Al-Ti-O inclusions were seen along with silicon. The wt% of the extracted inclusions for FeTi70 and FeTi35 was approximately 1 to 1.50 and 9 to 10 wt% respectively. The high amount of insoluble impurities in FeTi35 could be due to the presence of large amount of silicon/silica. This high amount of silicon/silica in FeTi35 can be attributed to its low grade starting raw material (ilmenite).



a) b) c)

Figure 3: Insoluble impurities obtained after the acid dissolution (a) FeMo (b) FeP (c) FeTi70

The extracted quantity of the insoluble impurities increase with ferroalloy grade by the order: FeP < FeMo < FeTi70 < FeTi35 (**Table 4**). This is roughly in agreement with the total oxygen contents of some of the ferroalloys (**Table 3**), suggesting that the total oxygen measured mainly present as the insoluble oxides in the ferroalloys and some of the oxides are soluble in acid. (2) The insoluble impurities found in the ferroalloys were mostly SiO_2, Al_2O_3 and in addition to these oxides, there was presence of Al-Ti-O in ferrotitanium grades. (3) Size of the residues and/or inclusions varies from 1 to 100 micrometers and distinct inclusion morphology, such as spherical, angular, faceted and irregular particles were observed. The examples of inclusion morphologies after extraction are shown in **Fig 3**. Spherical SiO_2 and irregular Al_2O_3 were found in FeMo alloy (**Fig.3 (a)**), angular (Fe, P, Mn, Ti)O_x complex in FeP (**Fig. 3(b)**), faceted Al-Ti-O inclusion in FeTi70 (**Fig. 3(c)**) and irregular Si/SiO_2 particles and Al-Ti-O in FeTi35 grade. These non-metallic compounds in the ferroalloys would be introduced to the liquid steel during alloying process, influencing steel cleanliness if these inclusions are not removed effectively.

Table 4: Insoluble impurities in ferroalloys after acid extraction

Ferroalloy	Composition (Phase)	Size, shape and morphology	Quantity (wt %)
FeMo	Si/SiO_2, Al_2O_3	Spherical (10 to 50μ)	0.50-0.90
FeNb	Not Any	-	-
FeP	(Fe, P, Mn, Ti)O	Angular (10 to 80μ)	0.30-0.40
FeTi70	Si/SiO_2, Al-Ti-O	Faceted (1 to20μ)	1.00-1.50
FeTi35	Si/SiO_2, Al-Ti-O	Irregular particles (1 to 50 μ)	9.00-9.50

3.3 Inclusions in the ferroalloys

Figure 4 shows how the impurities are bonded in the ferroalloys. The presence of SiO_2 in the FeMo (**Fig. 4(1)**) is in good agreement with the extracted inclusions. The microstructure of FeNb reveals two phases with apparently no inclusions (**Fig. 4(2)**). The presence of Al-Ti-O in FeTi70 grade is also in good agreement with extracted inclusions (**Fig. 4(3)**). The microstructures of FeP and FeTi35 were composition wise inhomogeneous especially the distribution of titanium and manganese in FeP and aluminium and rutile in FeTi35. In the micrographs shown in **Fig. 4(4)**, it can be deduced that the titanium oxide was not reduced completely by the aluminium during its production. The inhomogeneity in the microstructure of FeTi35, especially the uneven distribution of rutile can be seen at different locations. **Figure 4 (5a)** and **(5b)** shows the uneven distribution of two phases (A and B) in the FeP taken at the same magnification but at two different locations. The presence of Ti and Mn was found where the distribution of A-phase (P- 36.45 wt%) and B-phase (P- 24.93 wt%) is relatively wider as indicated by the dotted region in **Fig. 4 (5b)**. The relationship between the impurities observed in the ferroalloys and the manufacturing methods of the ferroalloys is more extensively discussed in section 4.1.

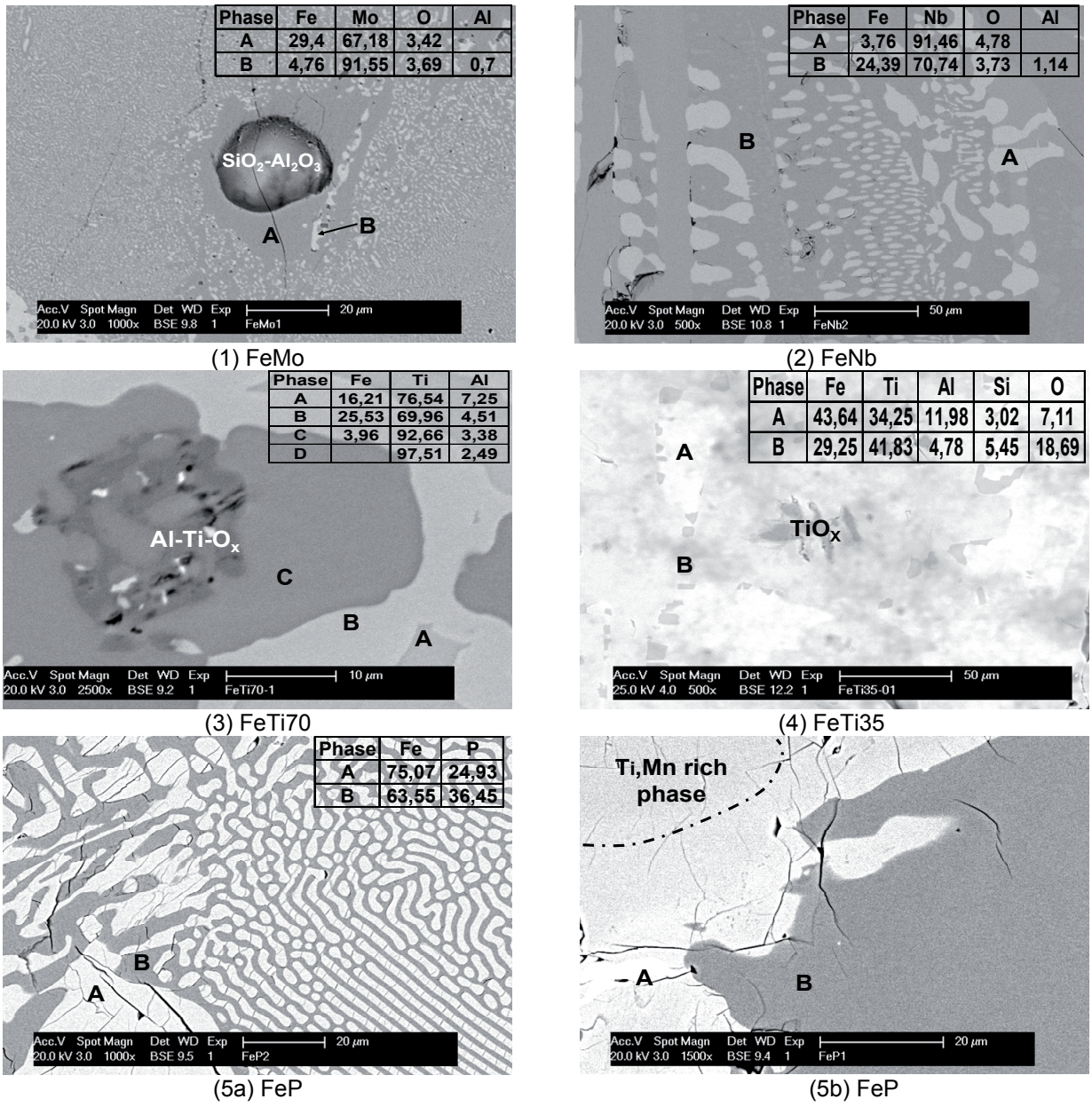


Figure 4: Microstructural features of (1) FeMo (2) FeNb (3) FeTi70 (4) FeTi35 (5a, 5b) FeP (The elemental composition of each phase as measured by EDS in wt% is shown in the tabular form)

4 DISCUSSION

4.1 Origin of Ferroalloy Impurity

The impurities present in the ferroalloys are linked to their starting raw material and the processing route. **Table 5** shows the various manufacturing routes of ferroalloy production. Depending upon the manufacturing route practiced as well as the ore (raw material) composition, presence of some impurities in the ferroalloys is unavoidable. This can be evident from the reactions given in the right hand column of the **Table 5**. The oxides which are formed during the reduction process were mainly found as the inclusions in the ferroalloys.

The inhomogeneity in the microstructure and the high amount of oxygen associated with FeTi35 as compared to FeTi70 is due to the different processing routes employed for the manufacture of these ferroalloy grades. The high grade FeTi70 is manufactured by alloying titanium sponge with iron while low grade FeTi35 is manufactured by the aluminothermic reduction of ilmenite and rutile. As mentioned in the previous section, the inhomogeneity in the microstructure of FeTi35, i.e. the uneven distribution of unreduced titanium oxide can be seen at different locations (**Fig. 4 (4)**). The higher total content of oxygen associated with FeTi35 (**Table 3**) can be attributed to such unreduced ore.

Table 5: Summary of ferroalloy production routes[9].

Ferroalloy grade	Raw material	Container / furnace / energy source	Manufacturing route
Ferromolybdenum	Mo concentrates (MoO_3), Iron ore, Al, Si	Self sustained process due to the exothermicity of Si, Al oxidation	Silicothermic reduction **$2/3MoO_3 + Si = 2/3Mo + SiO_2$** **$1/2\ MoO_3 + Al = 1/2\ Mo + Al_2O_3$**
Ferroniobium	Pyrochlore concentrate, columbite, iron oxide, lime, fluorspar, Al powder	Electric arc furnace	Aluminothermic reduction **$3Nb_2O_5 + 10Al = 6Nb + 5Al_2O_3$**
Ferrotitanium70	Titanium scrap, iron	Induction furnace / electric arc furnace	Alloying
Ferrotitanium35	Ilmenite, rutile, Al powder, potassium perchlorate, Calcined limestone	Refractory lined vessel or arc furnace	Aluminothermic reduction **$3TiO_2 + 2Al = 3TiO + Al_2O_3$** **$3TiO + 2Al = 3Ti + Al_2O_3$**
Ferrophosphorus	Phosphate rock, lime, carbonaceous material	Electric arc furnace	Byproduct of elemental phosphorus collected under slag

Ferrophosphorus is the byproduct of the elemental phosphorus production obtained by the carbothermic reduction of phosphate rock. FeP is collected under slag and further refined by means of oxidation in order to remove the impurities like Si, Mn and Ti. These elemental impurities originated from the phosphate rock can be present in the elemental form if they are not oxidized during the secondary treatment. This is exactly in agreement with extracted impurities (**Fig. 3b**) and the presence of Si, Mn and Ti in selected areas in the microstructure (**Fig. 4 (5b)**).

Therefore, impurities in ferroalloys can be present in elemental form or in the form of oxides/sulphides/nitrides or a combination of these as quantified from **Table 2** to **Table 4** and observed in **Fig. 3**. Apparently, as summarised in **Table 5**, the origin of these impurities in the ferroalloys is correspondingly correlated to their manufacturing routes

4.2 Evaluation of the Influence of Ferroalloy Impurities on Steel Cleanliness

Impurities in the ferroalloys can be estimated as total oxygen and sulphur, inclusions and other trace elemental impurities. Total oxygen and the extracted inclusions are inter-related as extracted acid-insoluble impurities are mostly oxides. This is substantiated by the present analysis results (**Table 3, Table 4 and Fig. 3)**.

In principle, impurities in ferroalloys can become a part of inclusions in the steel. But, it is quite unlikely for inclusions from ferroalloys to remain unchanged during the secondary steelmaking and solidification processes. In other words, at the steelmaking temperature and composition, it would depend upon the thermodynamic stability of the impurity element or inclusions as well as its residence time in the liquid steel to undergo any physical change (e.g., melting and/or dissolving) or chemical change (e.g., reacting with liquid steel to form new chemical compound). The formation of new compound would depend upon: (1). the availability of dissolved oxygen and sulphur in liquid steel. This oxygen or sulphur could be introduced to the liquid steel through the ferroalloys after deoxidation and/or desulphurization step. (2). The second possibility could be the replacement of the existing compound in the ferroalloy partly by the growth of new compound on the existing one e.g. precipitation of new inclusion on the existing one giving rise to dual phase inclusions[15-16]. In such a scenario, the inclusions introduced through ferroalloys can act as potential sites for the nucleation and growth of the newer inclusions in liquid steel resulting in the formation of complex compound e.g. the growth of Al-Ti-O inclusions are example of such phenomena. The already formed TiO_2 is partially replaced by the Al_2O_3 leaving Ti oxides in the core surrounded by the aluminium oxide[15, 17].

4.2.1 Total oxygen level in the ferroalloys

Apart from air infiltration, slag entrapment and the glazed refractories[18-19] of the ladle, the high amount of total oxygen present in some of the ferroalloy grades can contribute to the increase in the total oxygen content of steel. Total oxygen is approximately equivalent to the combined oxygen considering that solubility of oxygen in metals at room temperature is extremely low. The highest oxygen content was found in FeTi35. FeMo also has higher oxygen contents. Therefore, late addition of such ferroalloys can contribute to the increase in total oxygen content of the steel. The total oxygen content of the FeMo is not in agreement with the extracted inclusions leading to the possibility that some of the total oxygen is present in the form of molybdenum oxide which is soluble in acid. Molybdenum has less affinity towards the oxygen; therefore molybdenum oxide is most likely to get reduced by the other common alloying elements (e.g. Al, Si) in steel. In addition to this, as FeMo is added at an early stage because of its high melting point, this provides sufficient time for the flotation of inclusions formed in the above manner. Therefore, the contribution of total oxygen through FeMo can not be significant if used as a microalloying element.

Table 6: Cleanliness requirement for various steel grades[2].

Steel product	Maximum impurity fraction	Maximum inclusion size
Automotive & deep drawing sheet	[C]≤30 ppm, [N]≤30 ppm	100 µm
Drawn and Ironed cans	[C]≤30 ppm, [N]≤30 ppm, T.O.≤20 ppm	20 µm
Line pipe	[S]≤30 ppm, [N]≤35 ppm, T.O≤30 ppm	100 µm
IF steel	[C]≤30 ppm, [N]≤40 ppm, T.O.≤40 ppm	
HIC resistant steel (sour gas tubes)	[P]≤50 ppm, [S]≤10 ppm	
Ball Bearings	T.O.≤10 ppm	15 µm
Tire cord	[H]≤2 ppm, [N]≤40 ppm, T.O.≤15 ppm	10-20 µm
Alloy steel for pressure vessels	[P]≤70ppm	
Heavy plate steel	[H]≤2 ppm, [N]=30-40 ppm, T.O.≤20 ppm	Single inclusion 13 µm, cluster 200 µm
Wire	[N]≤60 ppm, T.O.≤30 ppm	20 µm

However, the contribution of total oxygen to the liquid steel through the introduction of FeTi alloys can be of importance considering that the Al-Ti-O inclusions present in FeTi are quite stable at steel making temperature. As FeTi alloys are introduced after complete deoxidation of liquid steel, it will provide less time for the flotation of such inclusions. According to the present analysis results (**Table 3**), the average total oxygen content in two ferrotitanium grades investigated viz., FeTi35 and FeTi70 were approximately 0.65 wt% (6476 ppm and 0.19 wt% (1859 ppm.) respectively. It means that, for IF (interstitial free) steel in which the titanium content varies between 400-600 ppm, the addition of FeTi70 would be 0.95 kg per tonne of liquid steel (for aim Ti content = 500

ppm, recovery assumed = 75%) which ultimately results in the contribution of 1.5 ppm to the liquid steel. If FeTi35 has to be introduced (for aim Ti content = 500 ppm, recovery assumed = 75%), the addition would be about 1.90 kg per tonne of liquid steel which results in the contribution of 12 ppm to the liquid steel. It could also further supplement the fact that the recovery which has been assumed the same for both the FeTi grades can not be the same considering the availability of a large amount of total oxygen immediately after its introduction. Such a high of amount of total oxygen in ferroalloys indicates the possibility of introduction of a large amount of inclusions. In this case, specific attention should be paid to inclusion control during the ladle refining and casting. **Table 6** shows typical steel cleanliness requirements reported for various steel grades. Depending upon the cleanliness requirements of a particular steel grade, the amount of the impurities like C, N, S & total oxygen (T.O.) introduced to the liquid steel through various grades of ferroalloys can be theoretically calculated. Another ferroalloy with higher total oxygen content (total oxygen~ 1400 ppm) is FeP. The possible origin of total oxygen is already discussed in the previous section 4.1. But, contrary to FeTi grades, FeP can be introduced before the deoxidation step providing more time for the removal of inclusions introduced in such a manner. The normal practice is to introduce FeP in the ladle after complete deoxidation. FeNb does not have significant amount of total oxygen present in it (**Table 3**).

4.2.2 Elemental impurities

Elements like calcium, titanium, aluminium, and magnesium play a crucial role in inclusion formation in the steel. The elemental composition of all the ferroalloys is given in **Table 2**. There is a variation in the individual elemental contents in each of the ferroalloy grades. The variation is wider especially in low grade ferroalloys like FeP and FeTi35. The elemental impurities present in significant amounts, are Al, V in FeTi70; Al, Ca in FeTi35; Ti, Mn, Ca in FeP and Al, Mg, Ca, Mo in FeNb.

Considering the various elemental impurities in the ferroalloys, their behavior would depend upon the affinity toward the available oxygen. Ca, Al, Ti, Si and Mn all have strong affinity for the oxygen as compared to V and Mo. Therefore, depending upon the quantity to be introduced to the liquid steel, the elements like V and Mo can be recovered without additional FeV or FeMo introduction. The elements like Al, Ti and Ca can form complex inclusions therefore, the exact quantity of these elements in the ferroalloy should be known before its introduction to the liquid steel. The formation of complex oxides or duplex (e.g., Al-Ti-O, oxysulphides) inclusions in the steelmaking processes depends upon the steel grade, which involves the specific ferroalloy combination, their amounts and the sequence of addition.

The presence of comparatively high amount of elemental aluminium in ferroalloys like ferrotitanium (**Table 2**) make them promising as this aluminium can possibly be used for deoxidation. However, the possibility of Al introduction as a deoxidizer, in such a manner has to be examined through planned trials as Al and Ti complex deoxidation has an impact over the morphology of the resulting inclusions[15, 17]. Approximately, 2-3 wt% and 4-5 wt% of aluminium were present in the analyzed FeTi70 and FeTi35 respectively (**Table 2**). The microstructure of FeTi70 revealed the presence of aluminium in all its phases as shown in the **Fig. 4 (3)**. In contrast, there was titanium oxide surrounded by Fe-Ti-Al phase in FeTi35 (**Fig.4 (4)**). This leads to the possibility that elemental aluminium in FeTi35 would be mostly consumed in reducing the unreduced titanium oxide and forming Al-Ti-O inclusions through the reactions shown in **Table 5**.

The possibility of impairing steel cleanliness through ferroalloy introduction will increase if 1) the ferroalloy is low grade i.e. the amount of base metal in ferroalloy is lower e.g. FeP and FeTi35, 2) the requirement of the base metal is high in steel chemistry so that quantity of ferroalloy to be introduced would also be high, 3) the ferroalloy is added to the liquid steel after the deoxidation providing insufficient time for the removal of inclusions introduced through the ferroalloy e.g. FeTi are always added to the liquid steel after complete deoxidation for higher recovery of Ti, 4) high in impurities i.e. available oxygen and sulphur contents, inclusions, and elemental impurities particularly those elements which even in smaller amounts can affect the inclusion formation e.g. Ca and Mg.
Therefore, in order to evaluate the influence of the ferroalloy impurity on the steel cleanliness, all of the factors need to be considered to indicate the influence of ferroalloy impurity over the steel cleanliness.

5 CONCLUSIONS

Considering the complexity of the steelmaking process as well as variation and inhomogeneity in the composition of the ferroalloys, the direct evidence of the influence of ferroalloy impurities over steel cleanliness may not be easily evident on the basis of characterisation of ferroalloys alone. Yet, the information obtained in

the present study can provide a link between the ferroalloy quality and steel cleanliness. We give the following conclusions to this work:

1. The inclusions in the ferroalloys were mostly the oxidized product of the reductant used to reduce the ores during the manufacturing of the ferroalloys. The relationship between impurities in the ferroalloys and its manufacturing route was established on the basis of extracted and observed impurities in the ferroalloy.
2. Considering some of the oxides and oxysulphides are soluble in acids, there was a good agreement between the inclusions observed in the microstructure and the inclusions obtained by the extraction technique. However, the extracted inclusions were not in complete agreement with the total oxygen content.
3. As the influence of ferroalloy impurity over steel cleanliness depends upon the number of factors as discussed, therefore, controlled alloying experiments need to be carried out to understand the influence of quality of each ferroalloy grade over steel cleanliness for a particular steel composition.

Acknowledgements

This work was performed with the financial support of ArcelorMittal Industry Gent (Sidmar) and the IWT (project no. 070277)

REFERENCES

[1] Kor, G. J. W., Claws P. C., Steelmaking and Refining volume (Pittsburgh, The AISE Steel Foundation), (1998), Chapter 11.
[2] Zhang, L., Thomas, B. G., ''State of the art in evaluation and control of steel cleanliness'', ISIJ Int., 43 (2003), pp. 271-291.
[3] Zhang, L., Thomas, B. G., Cai, K., Cui, J., Zhu L., ''Inclusion investigation during clean steel production at Baosteel'', ISS Tech Conf. Proc., ISS-AIME, Warrendale, PA, 2003, pp.141-156.
[4] Wijk, O., Brabie, V., ''The purity of ferrosilicon and its influence on inclusion cleanliness of steel'', ISIJ Int. 36 (1996), pp. 132-135.
[5] Sjoqvist, T., Jonsson, P., Grong, O., ''Inclusions in commercial low and medium carbon ferromanganese'', Metall. Mater. Trans. B, 32A (2001), pp. 1049-1056.
[6] Sjoqvist, T., Jonnson, P., ''Effect of ferromanganese additions on inclusion characteristics in steel'', 57th Electric Furnace Conf. Proc., Iron and Steel Society/AIME, (1999), pp. 383-393.
[7] Sjoqvist T., 'Influence of ferrochromium and ferromanganese additions on inclusion characteristics in liquid steel', PhD thesis, Royal Institute of Technology, Stockholm, Sweden, 2001.
[8] http://www.midwestnpioneer.org/oldsite/central/ltv.html
[9] Handbook of Extractive metallurgy edited by Fathi Habashi (1997) volume I part II
[10] Designation: E 194-90, Annual Book of ASTM standards, 03.05 (1992), pp. 428.
[11] Thomas, B. G., Bai K., ''Tundish nozzle clogging- application of computational models'', 18th Process Technology Division Conf. Proc., Iron and Steel Society, Warrendale, PA, 18 (2001), pp. 895-912.
[12] Abdelaziz, S., Megahed, G., El-Mahallawi, I., Ahmed H., ''Control of Ca addition for improved cleanness of low C, Al killed steel'', Ironmaking steelmaking, 36 (2009), pp. 432-441.
[13] Chang, C.-H., Jung, I.-H., Park, S.-C., Kim, H.-S., Lee H.-G., ''Effect of Mg on the evolution of non-metallic inclusions in Mn-Si-Ti deoxidised steel during solidification: experiments and thermodynamic calculations'', Ironmaking Steelmaking, 32 (2005), pp. 251-257.
[14] Feng, C., Cai-fu, Y., Hang, S., Yong-quan, Z., Zhou X., ''Effect of magnesium on inclusion formation in Ti killed steels and microstructural evolution in welding induced coarse grained heat affected zone'', J. Iron Steel Res. Int., 16 (2009), pp. 69.
[15] Sun, M-K., Jung, I-H., Lee H-G., ''Morphology and chemistry of oxide inclusions after Al and Ti complex deoxidation'', Met. Mater. Int., 14 (2008), pp. 791-798.
[16] Choudhary, S., Ghosh, A., ''Thermodynamic evaluation of formation of oxide-sulphide duplex inclusions in steel'', ISIJ Int., 48 (2008), pp. 1552-1559.
[17] Vanende, M. A., Guo, M., Dekkers, R., Burty, M., Vandyck, J., Jones, P., Blanpain, B., Wollants P., ''Formation and evaluation of Al-Ti oxide inclusions during secondary steel refining'', ISIJ Int., 49 (2009), pp. 1133-1140.
[18] Beskow, K., Sichen D., ''Ladle glaze: major source of oxide inclusions during ladle treatment of steel'', Ironmaking Steelmaking, 31 (2004), pp. 393-400.
[19] Tripathi, N. N., Nzotta, M., Sandberg, A., Sichen, D., ''Effect of ladle age on formation of non-metallic inclusions in ladle treatment'', Ironmaking Steelmaking, 31 (2004), pp. 235-240.