INFLUENCE OF PRODUCTION TECHNOLOGIES ON STEEL CLEANNESS: A COMPARISON

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VPLYV VÝROBNÝCH TECHNOLÓGIÍ NA ČISTOTU OCELE: POROVNANIE

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Abstrakt

Príspevok porovnáva účinnosť troch rozdielnych technológií pri výrobe čistej ocele. Boli posúdené tri rozdielne aspekty čistoty ocele:

a. Odsírenie ocele,

b. Obsah, zloženie a morfológia sulfidických inklúzií,

c. Obsah, zloženie a morfológia oxidických inklúzií.

Najlepšie výsledky boli dosiahnuté technológiou, zahrňujúcou skujňovanie ocele vo vrchom fúkanom LD konvertore, predbežné odsírenie syntetickou troskou v panve v priebehu odpichu, hlbokú dezoxidáciu ocele v panve a spracovanie ocele prídavkami na báze vápnika, vháňanými do tekutej ocele systémom škandinávskej trysky. Dosiahla sa modifikácia sulfidu mangánu na sulfid vápnika, ako aj modifikácia oxidu hlinitého na vápenaté hlinitany. Konečný obsah síry v oceli bol pod 0,002 % hm..

Technológia tavenia ocele v elektrickej oblúkovej peci s následnou dezoxidáciou a modifikačným spracovaním v panvovej peci bola menej účinná, hlavne pre dosiahnutú úroveň dezoxidácie. Boli pozorované len počiatočné štádiá modifikácie sulfidov a len malá časť inklúzií oxidu hlinitého sa modifikovala na vápenaté hlinitany. Konečný obsah síry v oceli bol okolo 0,005 % hm..

Hlavným úžitkom technológie skujňovania pomocou kombinovaného fúkania bol nižší obsah kyslíka v skujnenej oceli. V tomto prípade nebolo robené žiadne modifikačné spracovanie. Obsahy oxidických a sulfidických inklúzií boli veľmi podobné tým, ktoré boli zistené v oceľových odliatkoch, produkovaných prvými dvoma technológiami.

Abstract

The contribution presents comparison of three different steelmaking technologies efficiency in production of clean steel. Three different aspects of steel cleanness are considered: Desulphurization of

steel; Content, composition and morphology of sulphide inclusions; Content, composition and morphology of oxide inclusions.

The paper deals with three different steel production and treatment technologies and their impact on cleanness of produced steel. The technologies are as follows:

1. Production of steel in top blowed LD converter and ladle treatment of molten steel by lime based additions driven into melt by Scandinavian Lancers system (LD - SL).
2. Production of steel in combined blowing converter and treatament of molten steel in ladle by inert gas bubbling (CBC).
3. Production of steel in electric arc furnace followed by molten steel treatment in ladle furnace (Al wire and CaSi core profile) (EAF LF).

Main features of each technology are shown in Table 1a,b,c. The use of each of three mentioned technologies and their impact on steel cleanness were already published by the authors [1,2,3]. The aim of this contribution is to compare the effectiveness of the three technologies in production of clean steel. Three aspects are described:

Desulphurization ability;

Content, composition and morphology of sulphidic inclusions;

Content, composition and morphology of oxidic inclusions.

Table 1a Example of EAF-LF process

	Composition, wt.%					
Sample	C	Mn	Si	P	S	Al
EAF	0,04	0,07	0	0,005	0,012	
LF 1st sample	0,06	0,28	0,10	0,006	0,011	0,010
LF 2nd sample	0,05	0,26	0,07	0,005	0,011	
LF 3rd sample	0,07	0,28	0,09	0,006	0,011	0,021
LF 4th sample	0,08	0,34	0,17	0,008	0,009	0,020
Cont. cast	0,08	0,45	0,32	0,011	0,007	0,021

Additions,kg		EAF		Total	LF		Total
coke	245			245			
lime	707	1006	647	2360	100		100
flux		200	151	351	50		50
FeMnC			200	200			
FeAl			105	105			
FeSi			110	110	80	80	160
Al profile					25	10	35
SiCa profile						45	45
C profile					10	10	20
anthracite	210			210			

BF slag	180	180

Melt weight 51540 kg

Table 1b Example of LD - Scandinavian Lancers process

	Composition, wt.%					
Sample	C	Mn	Si	P	S	Al
pig iron	4,55	0,51	0,77	0,060	0,017	
LD converter	0,05	0,19	0	0,005	0,013	
ladle after tapping	0,03	0,12	0	0,005	0,013	
ladle after 2 min of stirring	0,04	0,23	0,03	0,005	0,007	0,167
ladle after addition of 300 kg lime	0,03	0,23	0,03	0,007	0,003	0,091
ladle after addition of 600 kg lime	0,03	0,23	0,04	0,007	0,002	0,062
final composition	0,09	0,23	0,04	0,007	0,003	0,036

	Temperature,°C	a_O, ppm
pig iron	1338	
tapping	1686	
ladle after tapping	1657	3,17
ladle after 2 min of stirring	1643	3,56
ladle after addition of 150 kg of lime	1619	1,96
ladle after addition of 300 kg of lime	1608	2,03
ladle after addition of 450 kg of lime	1594	2,21
ladle after addition of 550 kg of lime	1590	2,33
ladle after addition of 600 kg of lime	1581	1,89
final	1578	1,61

	Additions, kg
tapping	400 CaF_2; 200 FeMnC; 380 Al; 1800 synthet. slag
Scandinavian	
Lancers	600 CaO
melt weight	190 000

Table 1c Example of combined blowing converter process

			Composition, wt.%					
Sample		C	Mn	Si	P	S	Al	
pig iron		4,45	0,54	0,77	0,070	0,070		
converter 1st sample		0,05	0,17	0	0,024	0,020		
converter 2nd sample		0,03	0,18	0	0,026	0,011		
ladle after tapping		0,04	0,19	0	0,008	0,012	0,056	
Fe	FeO	MnO	SiO_2	Al_2O_3	CaO	MgO	P_2O_5	S
slag	20,11	4,72	9,94	0,98	44,28	9,23	0,96	0,092

Converter additions,kg		ladle additions,kg	
coke	2050	FeMn	70
lime	13132	Al wire	40
flux CaF_2	310	Al block	270

Desulphurization of steel

When comparing three above mentioned technologies, the highest desulphurization rate was reached by the one using Scandinavian Lancers system. In fact, this technology consists of two desulphurization stages. The first one, the preliminary desulphurization, is carried out by synthetic slag in ladle during steel tapping from converter. Detailed study of this technology was described by the authors in literature [4]. Composition of syntethic slag was:61-66% CaO; 13,5% CaF_2; 10% Al_2O_3, 5% Al_{metal}, amount of synthetic slag added into 190 t steel melt was 1800 kg.

The second stage of desulphurization is carried out by lime based powder materials driven into steel melt in ladle by Scandinavian Lancers system. This technology resulted in steel melt sulphur content level about 0,002% wt or less. 600 to 800 kg of lime powder were added into 190 t steel melt in this case. Deoxidation of steel by Al wire prior to lime based desulphurization resulted in steel melt soluble oxygen content about 1 to 3 ppm. Final slag basicity in ladle was about 10 to 12, MnO+FeO content in slag was about 2% wt.

Desulphurization of steel melt by synthetic slag only, described in work [4], resulted in sulphur content not less than 0,005% wt. The higher desulphurization rate was not reached due to a minimal intersurface contacts between desulphurization agent (slag) and steel.

Similar desulphurization rate was reached by the technology carried out by lime based additions in the ladle furnace. The cover slag in the ladle had basicity between 3 and 6, FeO+MnO content in slag was about 1 to 2% wt. Total amount of lime based additions into 53 t steel melt in the ladle was up to 100 kg.

No special desulphurization treatment was carried out in steel melt produced in combined blowing oxygen converter process. Desulphurization efficiency of all three described methods is in Fig.1.

Fig.1 Desulphurization efficiency of three different technologies

Content, composition and morphology of sulphidic inclusions

Besides desulphurization one of the main goals of ladle treatment is modification of composition and morphology of sulphidic inclusions in steel resulting in better mechanical properties of steel.

The sulfide inclusions shape control index is expressed as 32/40. [%Ca]/[%S]. In steel treated by lime based additions with the help of Scandinavian Lancers system in ladle with sulphur content 0,002 to 0,005% wt and residual calcium content 20 to 30 ppm, the value of the index was about 0,5. The value 0,4 to 0,6 [5] indicates partial transformation of manganese sulphide to calcium sulphide. Microscopic examination of samples taken from cross-section of continuously cast slabs made of steel treated by above mentioned method, confirmed the presence of calcium sulphide (as a rim of calcium aluminates) along centre line. It means the local sulphide inclusion shape control index reached the value of 1,8 (when Ca/S>2), confirming the full sulphide modification.

Sulphide modification was influenced by manganese content in steel. Full sulphide modification requires manganese content less than 0,6% wt. Deep deoxidation of steel in ladle by Al wire prior to Ca-based additions treatment resulted in presence of MnS II inclusions. Microscopic examination of steel tube grades (higher manganese content) continuously cast slabs found MnS II inclusions on grain boundaries. Similar examination of deep drawing steel CC slabs (low manganese content) found MnS III and CaS inclusions. No considerable differences in sulphidic inclusions contents were found in both steel grades, Fig.2. Manganese content influenced manganese sulphide composition and morphology.

Fig.2 The influence of manganese content on quantity of sulphidic inclusions in steel

Low residual calcium content (20 - 30 ppm) in steel produced in electric arc furnace - ladle furnace system resulted only in initial stages of sulphide modification. Sulphidic inclusions in continuously cast steel blocks were mostly in form of MnS I. The low Ca/S ratio (less than 2) can lead to hydrogen cracking sensibility.

No desulphurization and modification ladle treatment was made in molten steel produced in combined blowing oxygen converter, resulting in higher sulphide inclusions content, Fig.3. Microscopic examination revealed MnS I and MnS - FeS sulphide inclusions in continuously cast slabs produced from such type of steel. The higher concentration of sulphide inclusions was found around centre line of slab cross-sections.

Fig.3 Comparison of sulphidic inclusions content in steel produced in CB converter and in steel treated by calcium based powder material

Forms of sulphide inclusions in continuously cast steel slabs and blocks, resulting from three studied technologies, are listed in Table 2.

Table 2 Sulphidic inclusions in continuously cast slabs and blooms

Production process	
CBC and treatment of molten steel in ladle by inert gas stirring	MnS I, MnS-FeS occurring separately or formed on grain boundaries
LD and ladle treatment by lime driven into melt by Scandinavian Lancers	
- with manganese content of 1,4%	MnS II occurring separately, CaS as a rim of $CaO.Al_2O_3$ - occasionaly
- with manganese content of 0,2%	MnS III occasionaly on grain boundaries, CaS as a rim of $CaO.Al_2O_3$ - occasionaly
EAF followed by molten steel treatment in ladle furnace (Al wire and CaSi profile)	MnS I occuring separately or formed along grain boundaries, $CaO.Al_2O_3$ - occasionaly surrounded by a CaS rim

Content, composition and morphology of oxidic inclusions.

Deep deoxidation of steel melt, carried out at the beginning of ladle metallurgy processes, was fundamental for all three studied technologies. Ratio between total oxygen content in steel and amount of oxide inclusions is depicted in Fig.4.

Fig.4 Oxidic inclusions content as function of oxygen content in steel

Different oxidation states of steel melt after refining in steelmaking furnaces were found in all three technologies: after refining in top blowed LD converter; after refining in combined blowing converter; after melting in electric arc furnace. Fig.5 compares the technologies from oxide inclusions concentration point of view. The inclusions were in fact alumina inclusions that resulted from aluminium killing of steel samples, taken from steel in the furnace. These inclusions replaced original FeO inclusions in steel melt in furnace.

Fig.5 Oxidic inclusions content in steel melts produced in three different steelmaking units

Lower oxygen content in steel melt in combined blowing converter, reflected by lower alumina inclusions content, resulted from easier elimination of CO gas from the melt due to the low partial CO pressure in bubbles of inert gas. Lower oxygen content in steel positively influenced iron content in slag and consumption of Al as deoxidation agent.

Composition of oxide inclusions in steel after deoxidation and alloying carried out during steel tapping reflected composition and amount of deoxidation and alloying agents. Only alumina inclusions, Fig.5, were found in deep drawing steel grades, manganese silicate and alumina inclusions in tube grades and steel melted in EAF. After deep deoxidation of molten steel in ladle by Al wire most oxide inclusions were in form of alumina inclusions.

The rate of Al_2O_3 modification to calcium aluminates was governed by Ca solubility, oxygen and aluminium activity in molten steel. Full modification was reached only in steel, treated by calcium based additions driven to steel melt in ladle by Scandinavian Lancers system.

Aluminium contents in steel melts in two subsequent technological steps, ladle and tundish of continuous caster, were compared. Two technologies were compared: steel treated by Scandinavian Lancers system in ladle and steel produced in electric arc furnace - ladle furnace system, Fig.6. As can be seen from the Figure, reoxidation rate reached values of 40 to 50% for both technologies.

Fig.6 Reoxidation rate at stage ladle - tundish in steel treated in LF and in steel treated by Scandinavian Lancers system

Morphology and composition of oxide inclusions in all three studied technologies are listed in Table 3.

Fig.7 shows nitrogen content values in studied casts. The nitrogen content in steel produced in EAF - LF is twice as high than the ones in steel made by converters. It is a result of fundamentals of the process (melting by electric arc) and of nitrogen blowing homogenization in the ladle furnace. Two others technologies used argon blowing into steel melt in ladle.

Table 3 Oxidic inclusions in continuously cast slabs and blooms

Production process	
CBC and treatment of molten steel in ladle by inert gas stirring	Mostly Al_2O_3 occuring separately or in clusters; occasionaly duplex inclusions of MnS - Al_2O_3
LD and ladle treatment by lime driven into melt by Scandinavian Lancers	Partly or completely modified $CaO.Al_2O_3$
- with manganese content of 1,4%	The centre line segregation moved up to loose side of the slab
- with manganese content of 0,2%	The centre line segregation found in the slab centre
EAF followed by molten steel treatment in ladle furnace (Al wire and CaSi	Globular silicates with additions of various oxides (MnO, Al_2O_3); uncompletely modified $CaO.Al_2O_3$

profile) inclusions

Fig.7 Nitrogen content values in studied casts

Conclusions

The aim of presented contribution was to compare efficiency of three different technologies in producing of clean steel. The technologies were described in details in three separate papers, published by the authors.

Three different aspects of steel cleanness were considered:

a. Desulphurization of steel;

b. Content, composition and morphology of sulphide inclusions;

c. Content, composition and morphology of oxide inclusions.

The best results were attained by technology comprising refining of steel in top blowed LD converter; preliminary desulphurization by synthetic slag in ladle in course of tapping; ladle deep deoxidation of steel followed by calcium based additions treatment, driven into molten steel by Scandinavian Lancers system. Both modification of manganese sulphide to calcium sulphide and modification of alumina to calcium aluminates were attained. Final sulphur content was below 0,002% wt level.

The technology of steel melting in electric arc furnace followed by deoxidation and modification treatments in ladle furnace was less efficient, mainly due to deoxidation level attained. Only initial stages of sulphide modification were observed and similarly, only small part of alumina inclusions was modificated to calcium aluminates. Final sulphur content was about 0,005% wt.

Major merits of combined blowing refining technology were low contents of oxygen in refined steel. No modification treatment was made in this steel. Contents of oxide and sulphide inclusions were very similar to ones found in steel casts produced by above mentioned technologies.

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