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Optimizing the effect of count and morphology of Alumina inclusions on enamel quality of ultra low-carbon Al-killed Steel

Enameling steel has important applications in our daily life as in domestic appliances and industry (chemical, agro-food, storage tanks, heat exchangers..etc.) due to its outstanding properties resulting from combined advantages of steel and enamel. The combination of such steel and enamel provides durability and glossy appearance that withstand chemical corrosion, abrasion, thermal shocks and fire. The durability and quality of enameling process depends to a great extent on the quality of substrate (enamel steel). To ensure an acceptable quality of such steel to be enameled, care must be taken during steelmaking and refining such grade to obtain low carbon levels (0.03-0.05%max) and minimum count of inclusions. The morphology of inclusions is adjusted by Ca-cored wire feed technology however melt stirring using Argon is very useful to minimize inclusions and gas contents. Vacuum decarburization of steel melt to ensure low carbon levels prevents the black specks during firing of such steel sheets; however micro-alloying with 0.2-0.5% Ti or V stabilizes the rest of carbon and creates default sites for hydrogen after cold rolling to prevent fish scale phenomena after enameling. Assessment of inclusion counts and their morphology as well as distribution of carbides are carried out using scanning field electron microscopy and ASTM standard.

1 . INTRODUCTION

The demand for cleaner steels is always targeted by the researchers every year. One of the most important steel categories that being used in our daily life and plays an important role in national economy is the enameling steel. It is applied in several fields of industry, even in the most corrosive atmospheres, as in the chemical and agro- food industries and in columns and heat exchangers. Its resistance to corrosion caused by combustion gases also makes it an excellent material for the manufacture of flue linings and exhaust manifolds. Enameling steel is widely used also in light engineering industries, as in electric household appliances, metallurgical and building industries as well [1, 2].

The chemistry of enameling steel contains low carbon and low silicon which permits a high level of oxygen and nitrogen gases to be dissolved in the steel melt [3]. The low carbon steels are widely produced for cold rolled sheets used for enameling. The high oxygen levels permits the formation of nonmetallic inclusions in the steel products hindering the rolling operation and the mechanical properties [4]. Aluminum is used extensively to kill the molten steel forming alumina (Al_2O_3) which can cause nozzle clogging during continuous casting, fatigue failure and deterioration of surface quality [5,6]. Non-metallic inclusions come from many sources including, deoxidation products, reoxidation products, slag entrapment and during improper ladle treatment [7,8]. Many researchers have studied the formation, removal and controlling the morphology of inclusions in the molten metal after deoxidation in the primary furnace and in ladle furnace [9,10]. The relation between a good slag and the removal of alumina clusters has been also studied by many researchers [11,12], however controlling the morphology of entrapped fine inclusions can be achieved by degassing, powder injection and cored wire feeding technologies [13-15].

The aim of this investigation is to study the influence of type and morphology of nonmetallic inclusions and nitrogen/hydrogen pick up on the mechanical properties of enameling steel and on the quality of enameled surfaces.

2. MATERIALS & TESTING PROCEDURE

In our investigation five steel materials have been delivered from Universal Group For Electric Appliances in Cairo as a case study to assess the count and morphology of nonmetallic inclusions as well as the dissolved

material	C	Si	Mn	S	P	Al	Ti	N
St.1	0.004	0.006	0.178	0.0038	0.0209	0.059	-------	0.0055
St.2	0.006	0.008	0.179	0.0034	0.0233	0.057	-------	0.0074
St.3	0.051	0.074	0.212	0.0097	0.0139	0.044	0.251	0.0102
St.4	0.109	0.065	0.423	0.0083	0.0182	0.033	0.210	0.0122
St.5	0.120	0.078	0.430	0.0091	0.0168	0.039	-------	0.0140

Table 1: Composition of the steel materials under investigation

nitrogen in the materials and to relate the results to the quality of final enameled products. The steel sheets are products of hot rolled CC slab strands and then cold deformed to 0.5mm gauge thickness. Table (1) shows the chemical composition of the materials investigated.

Steel No	2-5 µm	type	5-10 µm	type	10-30 µm	type
St.1	38%	Al2O3,CA	20%	Al2O3,CA,MnS	5%	CA MnS
St.2	42	Al2O3,CA	22	Al2O3,CA,MnS	7	Al2O3,CA,MnS
St.3	51	Al2O3,CA,TiC	29	Al2O3,CA,TiC	4	Al2O3,CA,TiC
St.4	58	Al2O3,CA,TiC	25	Al2O3,CA,TiC	6	Al2O3,CA,TiC
St.5	49	Al2O3,CA	32	Al2O3,CA,MnS	10	Al2O3,CA,MnS

Table 2: Distribution of non-metallic inclusions in St.1 to St.5

To evaluate steel cleanness longitudinal and transverse sections of the steel sheet were cut and polished and then examined using the traditional observations by image analysis (IA), metallographic microscopy (MM) and scanning electron microscopy (SEM).

Active oxygen measurement using probe sensors during steel making can give an approximate easy way to feel how the melt is clean, hence it can be controlled by equilibrium thermodynamics during deoxidation e.g. by aluminum as follows [16]:

$Log\ K = log\ ([Al]_2[O]_3) = -62780/T(K) + 20.54$

Accordingly if [Al%] = 0.03-0.06, the active oxygen could be 3-5 ppm.

The level of active and total oxygen in the steel could be a measure of the levels of nitrogen and hydrogen that can be picked up during steel making, refining outside furnace and during continuous casting due to the dissolution of entrapped air. Shrouding and submerged nozzle pouring during continuous casting of molten steel is a vital matter to prevent entrapment of atmospheric air into the molten steel.

3.RESULTS & DISCUSSIONS

3.1 Clean Steel

The average distribution percentage of and type of non-metallic inclusions per unit area (mm^2) of 10 fields of both longitudinal and transverse polished sections in the five steel samples St.1 to St.5 is summarized as in table (2).

It must be stated that the shown distribution of inclusions in the steel sheets under investigation reveals that the melts of these steels had been treated outside furnace by inert gas stirring and/or Ca treatment (powder or wire feed). The use of inert gas (Argon) stirring has an important role in control and floating the deoxidation products after heavy deoxidation with Al especially for these Si-poor low carbon steels. In such steel compositions it is very hard to avoid Al2O3 inclusions to a greater or lesser extent. The authors have studied already the effect of time (min) and rate of argon purging (Ndm3/min) into molten steel on the removal extent of Al2O3, calcium aluminates (CA) and Mns complex inclusions [17] as shown as in Fig.(1).

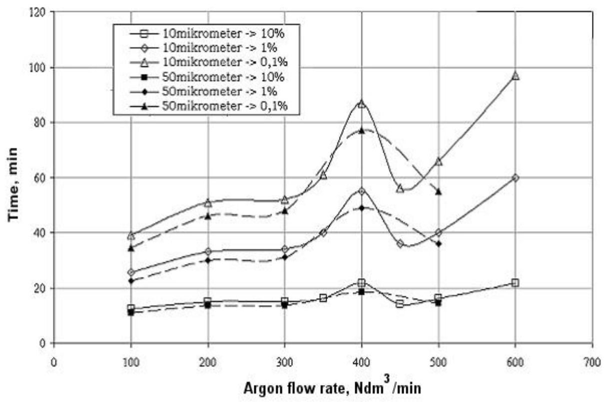


Fig.1: Time required to float inclusions quantity of 10,1 and 0.1% for sizes 10 µm, and 50 µm at different Argon flow rates

It was proved that mild stirring with 50-100Ndm3/min Argon is sufficient to remove impurities; however vigorous stirring with 300-500Ndm3/min is needed only for homogenizing stirring and reducing excessive temperature of molten steel before CC operation. The relative motion of both slag and molten steel depends to a great extent on the flow rate of Argon and the weight of the heat, providing that the Argon stirring must be

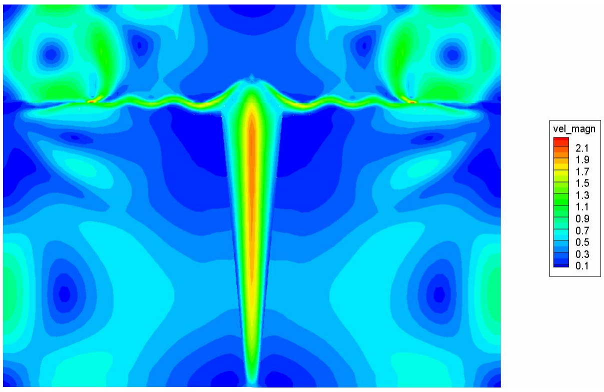


Fig. 2: Metal/slag flow regime during 50-100Ndm3/min Argon stirring

controlled not to eject the metal over the slag in the bulge region to avoid further oxidation by atmospheric air as shown in Fig.(2).

The physical and chemical composition of the slag must be adjusted to absorb and react with the floating inclusion constituents arising from the melt. Table (3) shows some technological parameters of heats produced at mild stirring.

Heat	(CaO) %	(Al2O3) %	(FeO) %	Al kg	Alwire kg	B	[O] ppm	[Al] %	Ar Nm3/min	Time min
1	57.5	28.3	2.4	220	60	8.23	2.56	0.05	225	20
2	58.3	25.7	2.3	243	55	10.4	2.63	0.06	185	18
3	62.3	25.7	3.6	225	60	9.32	3.32	0.04	201	22
4	53.6	23.5	2.9	210	20	7.85	2.12	0.05	230	21
5	61.5	29.4	3.1	198	10	9.91	4.56	0.04	190	17

Table 3: Technological parameters during Argon stirring of 150T heats

The second technology adopted was the cored wire (feed) Fig.(3), where a cored wire Al-wire filled with (CaSi, CaSiBa) fed into the ladle through a hole in the cover just at the end of the deoxidation and refining.

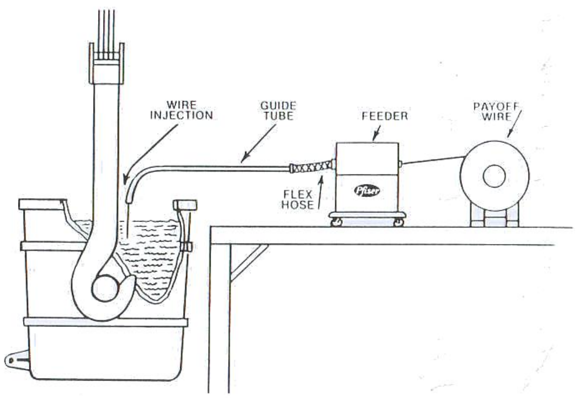


Fig. 3: Cored wire feeding system assembly

The equipment installed consists of pay-off machine with one or two spools of cored wire and a feeder strand. The conditions for wire feeding are:

Feeding speed: 80-300 m/min
Argon flow: 80-100 L/min
Feeding time: 2-3 min (depends on the melt analysis)
CaSi: 0.2-0.8 kg/ton
Ca yield: 9-11 %
Ca content: 10-18ppm

The cored wire feed is an efficient technology for desulphurization, insitu deoxidation and sulphide-oxide inclusions shape control. Feeding such a wire with that speed, insures suppression of Ca-boil due to the near bottom reaction.

Taking into consideration the above mentioned technological parameters, cored wire feeding proved to be more reliable and is in use all over the world hence the wire is preheated in the bath first and the reagents melts at the bottom rapidly. The effective solubility of Ca in steel melt is 30-60 ppm, however even 5-10 ppm Ca is capable to remelt the aluminates till reaching the formula CA (7Al2O3.12CaO) (Fig.5) in the middle part of inclusions besides changing the morphology of oxide, while the morphology of sulphides is also changed by Ca-treatment to form CaS which is concentrated around CA inclusions.

In a steel bath not containing Ca, the MnS appears as an individual liquid phase, the

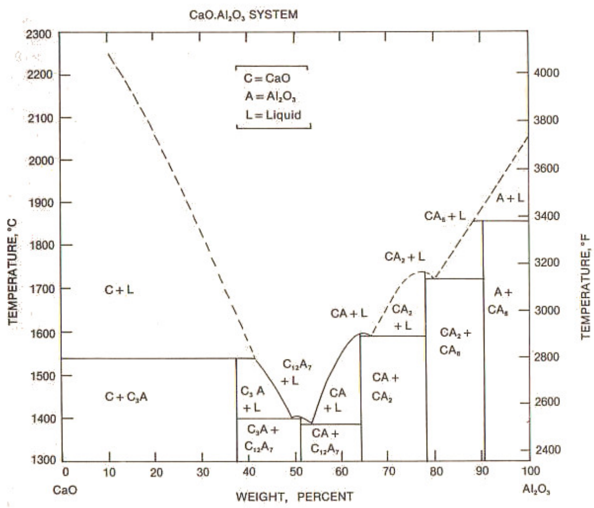


Fig. 5: CaO-Al2O3 equilibrium diagram

(CaS) appears as Ca added providing that Ca is exhausted first to form Aluminates as solid inclusions , and then they are covered by Mn-Fe-Ca-sulfides Depending on the increasing quantity of Calcium. Solid phase of (CaS) appears only in case, if liquid aluminates developed by increasing the Calcium addition and the excess can be exhausted as CaS and CaO as shown in Fig.(4).

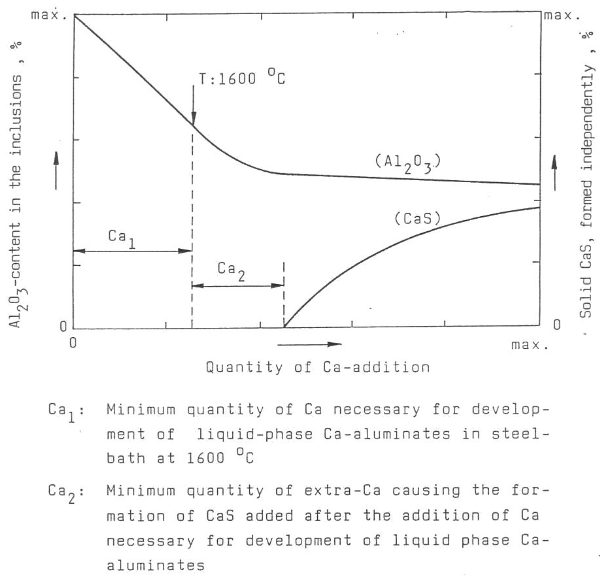


Fig. 4: Dependency of Ca addition and the equilibrium formation of CaS and Ca-Aluminates

3.2 Influence of Inclusions and gases on Enameling Quality

The success of the enameling process depends to a great extent on the quality of steel sheet used, however interstitial free (IF) steel is required to obtain defect free enamels. IF steel has excellent formability and always is produced through vacuum oxygen decarburization (VOD), precaution slab casting, hot rolling, coiling, deep cold drawing, annealing and then slicing or recoiling.

The phenomena of enamel black specks which appear due to firing and break down of carbon to form gaseous oxides that volatilize up through the molten enamel during firing leaving blow holes and specks behind as in Fig.(6a-c).

For that reason the carbon content recommended to be less than 0.008% as in case of St.1 and St.2 which shows excellent final enamel appearance. However, without micro alloying with Ti, steel sheets St.3 and St.4 samples which have (0.05%C) and (0.11%C) respectively show very bad enamel surfaces. Meanwhile, adding 0.2-0.25%Ti to St.3 and St.4 helped to combine and stabilize the unavoidable excess carbon and nitrogen to form TiC and TiN which are stable at firing process. Adding to that, the voids created in the steel structure by TiC and TiN during rolling become indeed a pockets to absorb hydrogen and decrease its pressure.

The phenomena of fish-scale formation can be happened due to the coalescence of hydrogen entrapments generated from steel and the enamel moisture building up high pressure to leave the enamel surface causing damages and fish-scale and star defects Fig.(6a-c). Vacuum and refining steel melts decrease to a great extent the hydrogen pick up, meanwhile good and selected enamel materials together with precautions in preparatory surface treatment operations can decrease the hazard of those enamel defects.

Enameling quality of steel sheet St.5 which has 0.12%C and nitrogen content 140ppm is found to have many defects due to the increased carbon firing hazard and hydrogen pressure build up after cooling. This advocates that the addition of Ti to St.3 and St.4 at such carbon contents.

The overall effect of size and morphology of inclusions on mechanical properties of steel sheets St.1-5 is depicted in Table (4) in which the presence of Al2O3 hard fine particulates, MnS and carbides deteriorates the mechanical properties of the steel sheet, however the formation of CA is beneficial.

Meanwhile, it is observed that the finer microstructure helped in

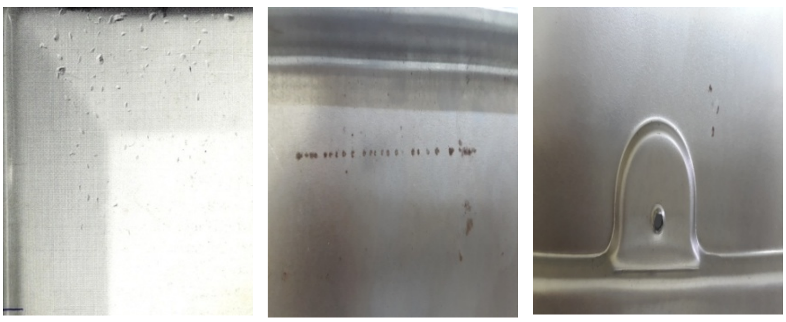

(a) Fish Scales (b) Black specks (c) Star blows

Figure 6(a-c): Enameling defects due to high carbon and nonmetallic-Inclusion in St. 4 & 5

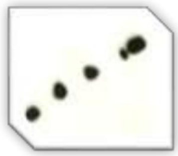
Steel sheet	Tensile(R_m) MPa	Yield(R_{eH}) MPa	Enamel Defects	Inclusions type and shape
St.1	310	245	Clean appearance	Globular CA 
St.2	300	230	Clean appearance	Small globules CA 
St.3	349	265	Clean appearance + !!!	Elongated CA 
St.4	370	278	Carbon fire specks X X X	Elongated MnS, Al_2O_3 
St.5	305	263	Star,fish –scale & carbon fire X X X	Fragmented Al_2O_3 

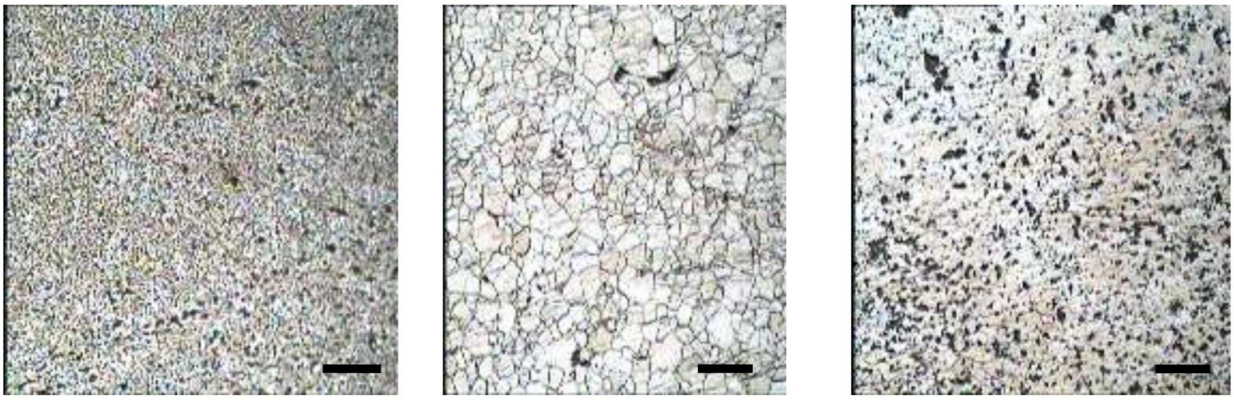
Table 4: Tensile strength of Steel sheets 1-5 and their inclusions type and morphology

increasing and improving the quality and productivity of the enameling line to a great extent and creating with Ti more free pockets as free traps for absorbed hydrogen. Fig. (7) shows the microstructures of St.1, 2, 3, 4 and its ferrite, carbide and some pearlite distribution.

The grain size of cold rolled steel sheet 1-2 is ultra fine and well distributed (ASTM No. 14), while steel sheet 3 is grain refined by cold rolling and Ti addition but its grain size is about No.9 due to higher finishing temperature (790°C). Steel sheet 4 has more carbides over St.1,2,3 although its grain size is fine (No. 11). The finer structures proved to have better mechanical properties and good enameled surfaces, however enameling of St. 4 and specially St.5 proved to have many defects as in Fig.(6a-c).

Conclusions

- low Carbon, minimum inclusion size and count as well as N and H gas contents determine the extent of success of plain carbon hot and cold rolled steel to be enameled.
- Addition of Ti (0.2-0.25%) to low-Si plain steels having C (≥0.05%) forms TiC and TiN precipitates creating active sites or pockets in which hydrogen is entrapped or locked instead coalescence and explode throughout the vitrified enamel layer causing defects named star blows.
- Controlling the count, size and morphology of Alumina inclusions in the steel melt by Argon stirring and Ca-wire feed, as well as the grain size of ferrite of the final steel sheet improves the quality of enameled steel surface.



St.1, 2 (fine α+ρ), 100μm St.3 (α+ρ), 100μm St.4 (α+ρ+TiC), 100μm

Figure 7: Microstructures and grain size distribution of St. 1, 2, 3, 4

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