INTERNAL QUALITY CONTROL OF STEELS DURING STEELMAKING AND CASTING FOR SOUR SERVICE APPLICATIONS AT ARCELORMITTAL LAZARO CARDENAS, MEXICO[1]

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Abstract

Steels for sour service applications demand stringent internal cleanliness control both in terms of non-metallic inclusions and dissolved gas contents. With the advances in steelmaking and casting processes, steel cleanliness has improved significantly over the last two decades. However, for line pipe steels for sour service applications, oil and gas companies are asking extra quality requirements to guarantee safety against hydrogen induced cracking during service. ArcelorMittal Lazaro Cardenas (AMLC) at Mexico has implemented key steelmaking and casting technologies to cater to the challenges of sour service slab making. The current article discusses some of the key process controls adhered to during steelmaking, casting and solidification that has enabled AMLC, Mexico to achieve effective resistance to hydrogen flaking in the skelp and excellent hydrogen induced cracking (HIC) resistance in the final product.

Key words: Hydrogen induced cracking (HIC); Segregation; Line pipe; Non-metallic inclusion.

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1 INTRODUCTION

There is growing interest among oil and gas companies in collecting crude oil and gas from sour (H_2S containing) reserves. Transportation of sour oil and gas from the well sites to the processing stations requires pipelines resistant to hydrogen-induced-cracking (HIC). Unlike line pipe steels for downstream distribution lines, HIC resistant line pipe steels mandate stringent internal cleanliness for prevention against any hydrogen buildup and subsequent delayed cracking.

A measure of successful HIC resistance of pipelines is usually assessed through standardized corrosion tests such as NACE TM 0284[(1)] on pipe or plate samples which evaluate the steel's susceptibility to HIC in reproducible service conditions. In order for steelmakers to guarantee minimal cracking in pipe samples during such standardized tests, care has to be taken from steelmaking stage itself so that the steel is extremely clean with regard to non-metallic inclusions, and free from centerline segregation and shrinkage cavities, as these are the most likely sites for accumulation and recombination of atomic hydrogen.[(2-4)] The harmful influence of hydrogen in steel is a continuous and cumulative process that sets in during solidification and continues during downstream processing. Stress gradients are known to provide driving force for atomic hydrogen to diffuse to discontinuities such as crack tips, matrix-inclusion interfaces, and other regions of high stresses/triaxiality. Once atomic hydrogen recombines to form molecular hydrogen, it can no longer be diffused out. Steelmaking and casting technologies are therefore needed to guarantee minimum refuge or sinks in the steel for the dissolved atomic hydrogen.

Inclusion shape control is the foremost requirements for sour service steels. Fine, isolated and globular inclusions such as Ca-aluminates and sulfides do not pose risk with regard to HIC,[(5)] but MnS inclusions and other non-metallic stringers/clusters often causes inclusion-matrix decohesion and stress concentration at the tip during hot rolling which facilitates hydrogen accumulation and crack initiation.[(2,3)] MnS inclusions are the last to be precipitated during solidification in the center-segregated region of slabs and are softer than the steel matrix. HIC resistant steels therefore, should have minimum possible S and any MnS inclusions formed should be made non-deformable through alloy-hardening with Ca during Ca treatment.[(6)]

Centerline segregation, caused mainly by segregation–active elements such as carbon, manganese, sulfur, phosphorus and oxygen[(7)] gives rise to hard transformation products in the mid-thickness of finished product providing an easy path for stepwise hydrogen induced cracking.[(3,8,9)] Centerline segregation is also primarily responsible for centerline porosity in continuous cast slabs.[(7)] These porosities are easy sinks for hydrogen that gets dissolved in steel during the steelmaking process. Porosities or cavities filled in with molecular hydrogen are difficult to annihilate during hot rolling and will exert high pressure resulting in cracking in rolled products.[(5)]

Minimization of hydrogen pick up during steelmaking and casting is also of utmost importance and is done through use of proper degassing technology, use of low-hydrogen Fe-alloys, dry casting and mold powder, preheated tundish and submerged entry nozzles (SEN).

Slow controlled cooling of slabs after solidification often drives out most of the atomic hydrogen from the system, since longer time is spent at temperatures where the diffusivity of hydrogen is high. It is reported that a final hydrogen content of 2 ppm and less in slabs is capable of delivering effective HIC resistance in thick gauge line pipe plates.[(5)]

This article discusses some steelmaking practices adopted in AMLC Steel Mill at Mexico for specific control of steel internal quality in terms of non-metallic inclusions for the production of HIC resistant steel slabs for linepipe applications.

2 STEELMAKING AND CLEANLINESS CONTROL

Production for sour service line pipe slabs initiated at AMLC during September 2011 for API X52, X60 and X65 grades based on customer orders from Europe, Asia and North America. AMLC also regularly produces API X70 grade non-sour slabs and the typical compositions of these grades are listed in Table 1.

Table 1. Composition of sour service line pipe steels cast, wt.%

Steel Grade	C, max	Mn, max	P, max	S, max	Al	Ti, max	N, max	Nb, max	Others
API X52	0.04	1.00	0.012	0.001	0.025-0.040	0.02	0.006	0.05	Ni
API X65	0.06	1.35	0.012	0.001	0.025-0.040	0.020	0.006	0.07	Cr, Cu, V
API X70	0.05	1.55	0.012	0.001	0.025-0.040	0.020	0.006	0.07	Cr, Mo

Steelmaking route followed was Electric Arc Furnace (EAF) – Ladle Furnace (LMF) - RH Vacuum Degassing. At EAF, 100% direct-reduced iron (DRI) pellets were used with 94% metallic content and very low S (0.002 wt.%) and P (0.06-0.08 wt.%). Near absence of residuals and low S, P contents of DRI ensured cleaner steel output from the EAF (220 T capacity).[10] In the ladle furnace, refining operation was carried out in a three-stage Ar-bubbling practice using multiple porous plugs. In the first stage, Fe-Alloy addition is accompanied by Al-deoxidization followed by lime addition for desulfurization. Ar-bubbling process lasted for about 20-22 minutes. Second stage of Ar-bubbling was carried out in a reduced blowing rate of ~20 Nm^3/hr for compositional control and alloy dilution in the melt. When the oxygen activity and S were reduced to very low levels at the end of second stage, gentle Ar-rinsing of the melt was introduced with metallic Ca-wire injection so that low melting Ca-aluminate inclusions are formed and were readily floated out of the melt. Only one porous plug with reduced Ar flow rate was used during this process so as not to disturb the slag layer and ease inclusion floatation. The Ca-treatment was also aimed at modifying MnS inclusions through alloying with Ca to form (Ca,Mn)S, which is non-deformable at hot rolling temperatures. Care was taken not to exceed a Ca:S ratio of 3.5-4.[9]
All the line pipe heats were treated at the RH vacuum degassing station for N and H removal. Though AMLC has both RH and Vacuum Tank degassers, sour service heats were treated at RH station because of more effective and faster H and N removal.[10] H and N could be reduced to under 2 ppm and 30-55 ppm, respectively, at the end of RH degassing.

3 CASTING AND SEGREGATION CONTROL

Steel casting technology and critical process control strategies for production of line pipe grades at AMLC have been published earlier[11,12] but salient features of AMLC continuous casting unit are two twin slab casters of which one is equipped with dynamic soft reduction (DSR). All linepipe grades are routed through the caster with DSR. Slabs were cast in sections of 250 mm thickness and 1.900 mm width. Based on grades of steel and detection of solidification point using a Dynamic Solidification Control (DSC) model, typically 3-6 mm total soft reduction, was applied to control centerline segregation and solidification shrinkage. The following process controls were strictly employed during the casting process:

- preheated SENs and tundish;
- ar-circulated ladle shroud ring between ladle to tundish;
- dry mold powder;
- use of stopper rod in place of slide gate;
- superheat of less than 25°C.

Dissolved hydrogen was measured on samples from tundish melt. After the slabs were cut to predetermined lengths, samples were cut from slabs for macro etch tests for slab centerline quality assessment and subsequently taken to a slow cooling station for controlled cooling for further removal of hydrogen.

3 RESULTS

3.1 Slab Internal Quality – Macrostructure

Figure 1a shows full width transverse macrographs of macroetched slabs from steel grade API X65 for sour service. Transverse macrographs of API X70 non-sour slabs are also presented in Figure 1b. Macroetching was done using 30% HCl aqueous solution.

(a)

(b)

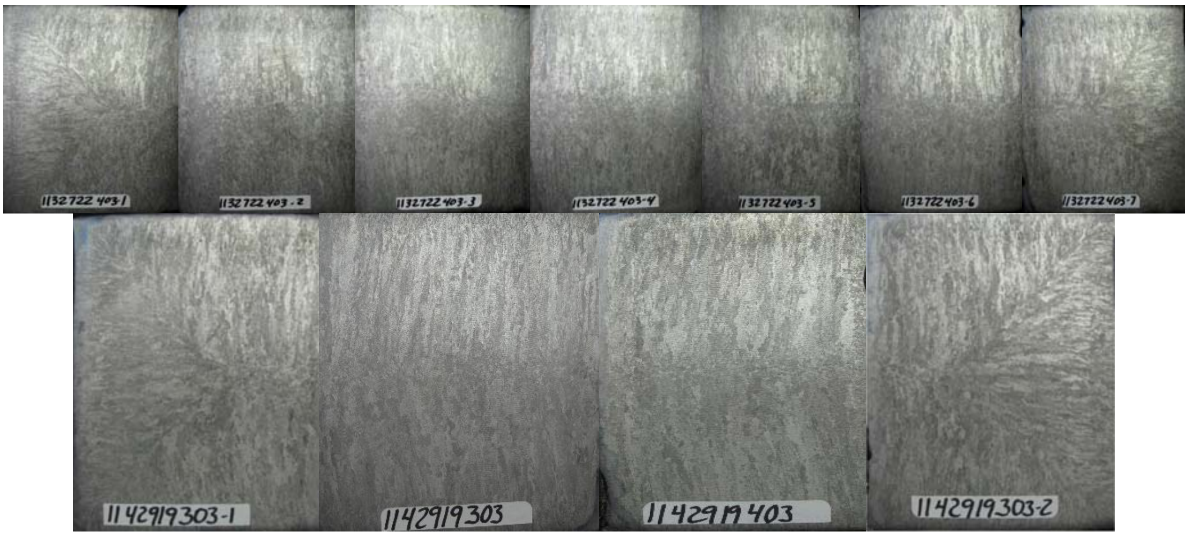


Figure 1. Transverse section macrographs of (a) API X65 sour slabs and; (b) API X70 non-sour slabs after macroetching revealing clean centerline conditions with no shrinkage cavities.

Macrographs of both line pipe grade slabs indicate columnar grains extend almost to the center of slab with no equiaxed zone at the center. No indication of centerline chemical segregation[10] or shrinkage cavities could be observed in either steel grade~~s~~. API X70 grade slab macrographs have been presented to indicate quality of centerline regions obtained with higher Mn contents (1.55 wt.%). The macrographs clearly indicate sound internal conditions of the steel grades cast and effective application of soft reduction in minimizing chemical segregation.

3.2 Slab Internal Quality – Microstructure

API X65 sour slabs were processed to 20 mm thick TMCP plates and subsequently to 36” OD LSAW pipes[13] and API X70 grade non-sour slabs were processed to 9.5 mm HR coils at customer’s end. Metallographic evaluation of internal microscopic quality was carried out on samples collected from final products.

(a)
(b)

Figure 2. Hot rolled microstructures of (a) API X65 sour pipes; and (b) API X70 HR coil samples at mid-thickness regions revealing no banded structure of hard transformation products. The microstructures are compared with corresponding slab macrostructure after macroetching. Etched with 2% Nital.

Figure 2 presents microstructures at mid-thickness regions of API X65 pipe sample and API X70 HR coil sample. The microstructures are compared with corresponding macrostructure of the mother slabs at central thickness. API X65 pipe sample revealed a fine ferrite-pearlite homogenous microstructure with no banded structure or hard transformation products, thereby manifesting near-absence of chemical segregation. API X70 HR coil microstructure showed a mixed acicular-polygonal ferrite grains with no centerline segregation or banded hard transformation products either. However, some M-A constituents could be observed along the centerline regions between grain boundaries but they did not appear as bands. Appearance of hard microconstituents is mostly a function of alloy design and hot processing practice.[8,9,14] Nonetheless, the clean centerline conditions in line pipe quality slabs presented in Figure 2 undeniably demonstrate effective casting practice employed.

3.3 Slab Internal Quality – Inclusion Contents

Figure 3a presents typical unetched microstructures of API X65 sour pipes and API X70 non-sour HR coils revealing general shape, size and distribution of non-metallic inclusions observed in these steels. Both the steels revealed very clean microstructures with regard to non-metallic inclusions. Inclusions were very fine and globular as shown in Figure 3a and no clustering or stringers were found. SEM-EDS microanalysis showed globular inclusions to be mainly fine Ca-aluminate and duplex (Ca,Mn)S-Ca aluminate. Occasional isolated CaS-MnS inclusions were also found. Figure 3b shows SEM micrograph of typical Ca-aluminate inclusions mingled with (Ca, Mn)S inclusions and EDS microanalysis indicating elements present. Presence of Mg was also found within these complex inclusions. Size of most of the Ca-aluminate and oxide-sulfide conglomerate was less than 2 μm. Energy dispersive X-ray mapping of such Ca-aluminate inclusions presented in Figure 4 revealed presence of very low amounts of Mn. This was also observed in the case of a few isolated (Ca,Mn)S inclusions (Figure 5) and was mainly due to very low levels of S (<0.001 wt.%) in the steels. Isolated CaS-MnS inclusions were found to be rich in Ca and thus rendered them undeformable due to alloy-strengthening at hot processing temperatures[15] (Figure 5).

Inclusion distribution was quantified using ASTM E45-11 standard.[16] The inclusion rating given in Table 2 indicates the presence of mainly globular oxides. Predominantly aluminate inclusions are listed under Type B and Ca-aluminate-only inclusions are listed as globularized Type D. Clearly the inclusion rating is consistent with the very clean microstructures observed in the steels.

Table 2. Inclusion rating as measured in both steel grades

Steel Grade	Type A Sulfides		Type B Alumina		Type C Silicates		Type D Globularized Oxides	
	Thin	Heavy	Thin	Heavy	Thin	Heavy	Thin	Heavy
API X70	0	0	0.5	0	0	0	1	0.5
API X65	0	0	0.3	0.2	0	0	0.4	0.3

(a)

(b)

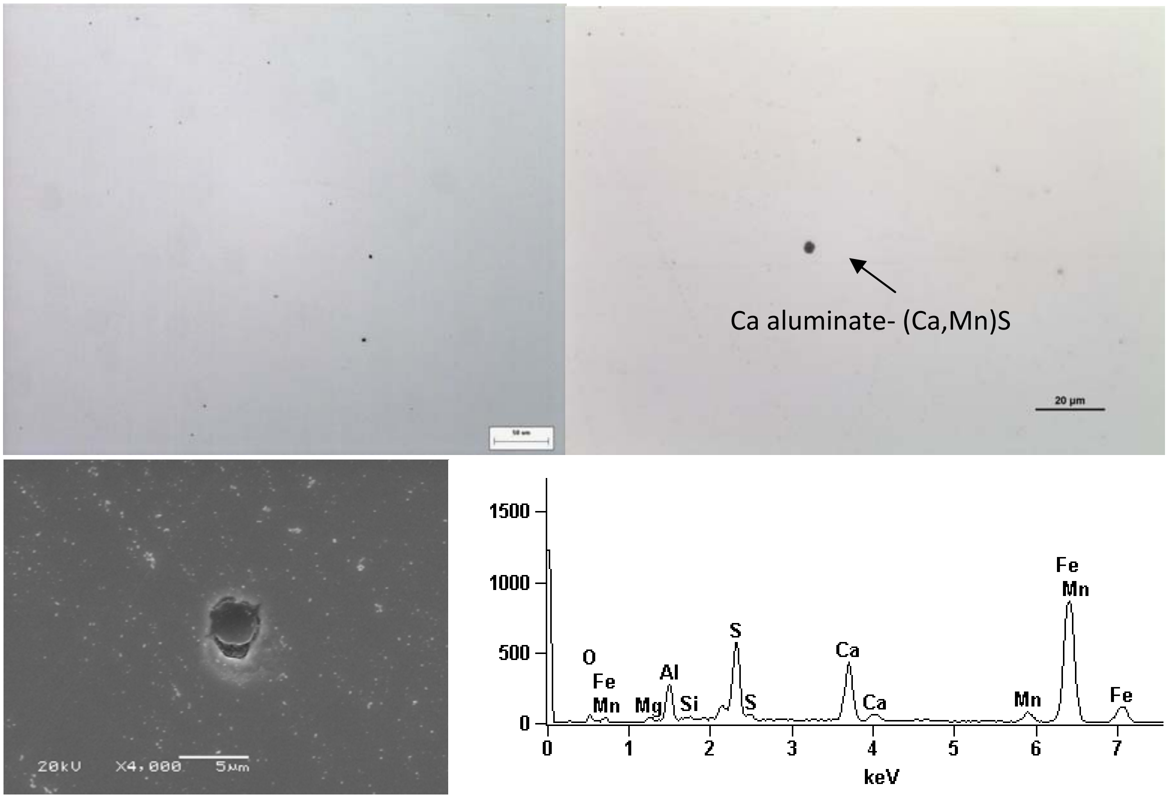
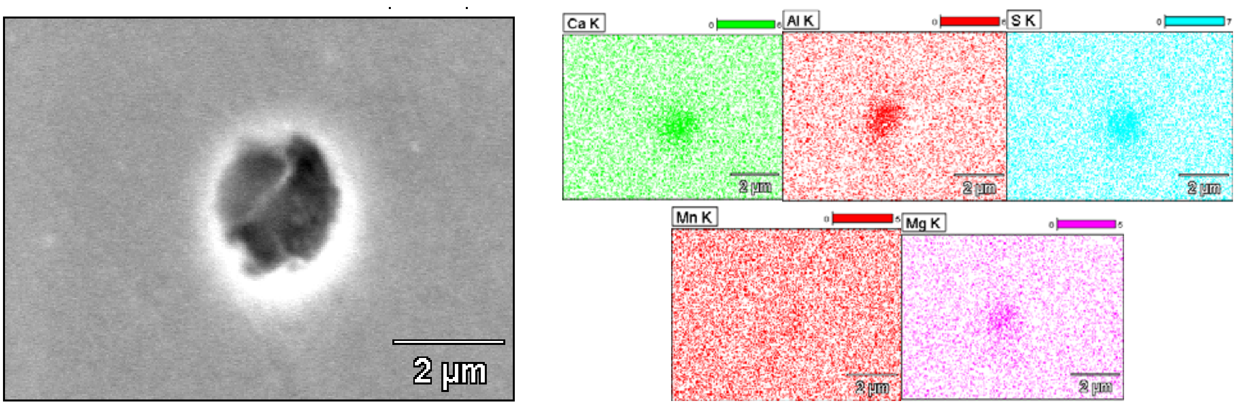
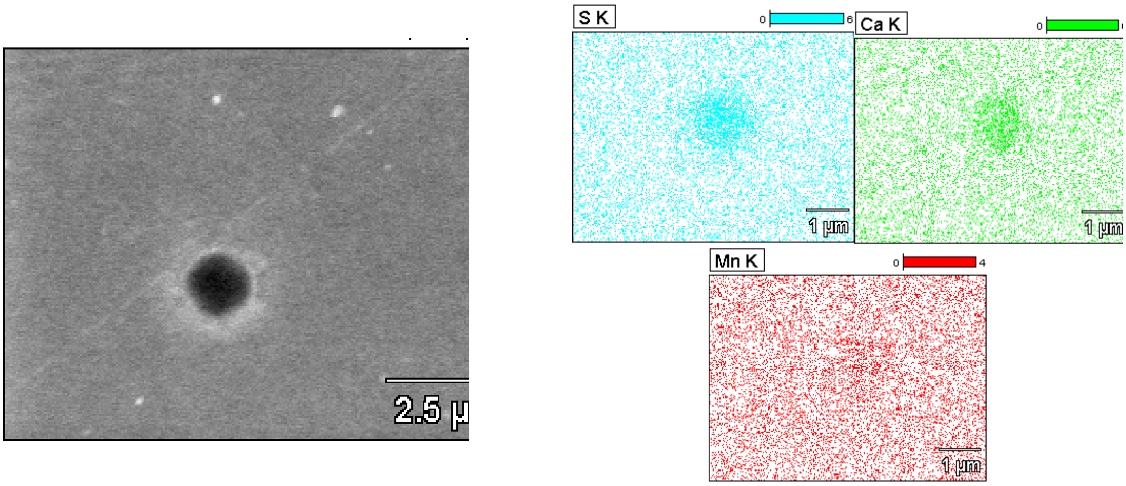


Figure 3. (a) Typical inclusion contents and distribution in line pipe grade heats. The inclusions are mostly oxide-sulfide conglomerate as shown in SEM-EDS microanalysis in (b) and were not deformed after hot processing.



(a) (b)

Figure 4. (a) Duplex Ca-aluminate and (Ca,Mn) sulfide inclusions of less than 2 μm in sizes were observed in the steels. (b) Energy dispersive X-ray mapping indicated very low amounts of Mn present in the inclusions. Presence of Mg is also indicated and can be related to pick up from slag.



(a) (b)

Figure 5. Isolated, globular, undeformed (Ca,Mn)S inclusions found in the steels with significant alloying by Ca as reflected in the X-ray mapping.

3.4 Hic Tests

It is worthwhile to mention that the API X65 sour plates were examined ultrasonically before and after pipemaking and did not reveal any internal discontinuities.[13] Hydrogen induced cracking susceptibility tests were conducted on API X65 plate and pipe, and API X52 grade pipe samples (6.25 mm wall thickness) as per NACE TM0284 specification[1] using Solution A ($2.7_{initial} \leq$ pH $\leq 4.0_{final}$). After the tests, samples were examined under optical microscope for appearance of cracks followed by ultrasonic testing. None of the plate or pipe samples revealed microscopic cracks due to hydrogen resulting in 0% CLR (crack length ratio), CSR (crack sensitivity ratio) and CTR (crack thickness ratio).

4 SUMMARY AND CONCLUSIONS

Steelmaking and process controls were effectively employed to control internal cleanliness of steels for sour service and also for non-sour service line pipe applications. Inclusion characterization revealed clean microstructures of the linepipe steels cast and only globular inclusions could be observed with size mostly less than 2 µm. Ca-treatment could be effectively introduced to induce fine globular Ca-aluminate inclusions and many times jointly with (Ca,Mn)S. Some traces of Mg was found in aluminate-sulfide combo inclusions which may be due to pick up from the slag.[15]

Isolated sulfide-only inclusions were occasionally found such as (CaS-MnS). These sulfides were found to be rich in Ca and hence could strengthen significantly so that they remained globular after hot processing. Ca enrichment of sulfides is also suggestive of very low S content of the steel.[17]

Controls on effective dynamic soft reduction guaranteed least centerline segregation in line pipe slabs even with higher Mn-contents and thus formation of centerline band of hard microstructural constituents in the final hot rolled products could not be observed. Introduction of 100% DRI use in EAF steelmaking ensured lowest S, P contents in the steel which also contributed in minimizing centerline segregation in such critical steel grades.

HIC tests under severe environmental conditions did not give rise to any microscopic cracking which could be attributed to the globular non-metallic inclusions and near absence of the harmful influence of hydrogen. It remains to be seen how the acicular ferrite microstructure in API X70 grade HR coils will respond to HIC tests given the clean centerline conditions and cleanliness from non-metallic inclusions but the results of the API X65/X52 plate and pipe samples undeniably suggest inclusion shape control and clean centerline are key to successful performance in HIC tests.

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