Niobium Bearing Structural Steels
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SOME ASPECTS IN THE PRODUCTION OF MICROALLOYED STEELS

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Abstract

Continuous casting has been a primary process innovation in the steel industry from the 60´s to the 80´s of the last century. This technology led to dramatic improvements in the productivity of the steelmaking process and in the quality of products. However, for keeping steel materials competitive and cost effective, an all-embracing approach of the steel making process is required. The whole manufacturing path from hot metal and/or melting through refining to casting through to the rolling and finishing has to be put under integrated control.

In regard to continuous casting, two examples of this trend are: improvements in tundish design and metallurgy, optimized submerged nozzles and high performance mold level control. The never-ending search for clean steel has shifted from the caster itself to ladle metallurgy. In the same way, the search for a defect-free surface is not simply focused on continuous casting technology, but also takes steel making into account.

With structural steel grades changing alloy design from plain medium carbon-manganese to crack-sensitive low carbon micro-alloyed HSLA modern steel, continuous caster design and technology stayed abreast of changes. However, it remains the foremost responsibility of steel plant operations and operation's maintenance to keep the equipment in excellent condition to produce defect free quality slabs.

Continuous Casting History

Continuous casting (CC) was the major process innovation in the steel industry from the 60´s to the 80´s of the last century. This technology led to dramatic improvements in the productivity of the steelmaking process and in the quality of products.

The world's first production oval-bow continuous casters with a cross section of 2.050 x 200 and 250 mm started in 1967 at Huettenwerke Krupp Mannesmann (formerly Mannesmannroehren-Werke) in Duisburg, Germany. Astonishingly, this caster is still in full operation (Figure 1). Due to the unique secondary cooling design-dry cooling (no spray-cooling at all) and newly designed support rolls, this caster is nearly exclusively used in the casting production of crack-sensitive micro-alloyed API steel grades for EUROPIPE's large-diameter pipe mill.

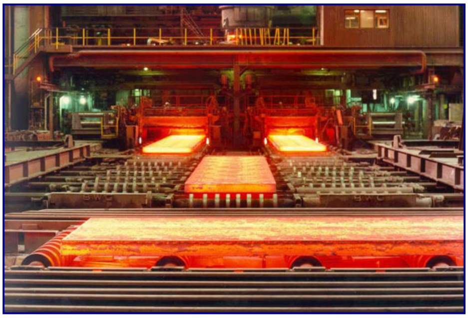

Figure 1. Twin-strand oval-bow continuous caster [1].

Between 1980 and 1990 Near Net Shape Casting (NNSC) emerged in continuous casting technology and became a success story in the manufacturing of commercial and special strip steel grades.

Schloemann Siemag (SMS) successfully tested their Compact Strip Production (CSP) in 1985. The first industrial application started in 1989 at NUCOR's Crawfordsville, Indiana plant. Up to this date there are about 40 near net shape (NNS) casters in full operation or under construction worldwide.

To supply the increasing demand for heavy plates, steel producers turned to thick-slab casting. In 1997, Dillinger Huette in Germany started the world's largest continuous-cast slab cross-section of 2.200 x 400 mm. The unique vertical caster with bending after complete solidification allows the production of heavy plates in excess of 100 mm and makes Dillinger Huette a specialist in supplying heavy steel plate for offshore industry, mechanical engineering, and for demanding structural applications. To participate in that lucrative heavy plate market, several steel producers are now investing in a thick-slab caster, e.g. Shougang Qinhuangdao Works/China (1.600 – 2.400 x 250, 400 mm), VoestAlpine Stahl/Austria (740 – 2.200 x 225, 285, 355 mm), and also Salzgitter Flachstahl, Salzgitter/Germany (1.100 – 2.600 x 250, 350 mm).

Excellent Steelmaking – Prerequisite in Producing Quality Slabs

In order to keep steel competitive and cost effective, a holistic approach to the steel making process is required. The whole steelmaking flow process from hot metal and/or melting through refining to casting, all along to rolling and finishing has to be put under integrated control. In regard to continuous casting, here are two examples of this trend [2]. After improvements in metallurgy and tundish design, optimized submerged nozzles and high performance mold level control, the never-ending search for clean steel has shifted from the caster to ladle metallurgy.

In the same way, the search for a defect-free surface is not simply focused on continuous casting (CC) technology, but takes alloy design and steelmaking into account.

The term "clean steel" is quite commonly used to describe steel that has:

- Low level of solute elements
- Controlled level of residual elements
- Low frequency of oxides created during steel making, ladle metallurgy, casting and rolling

The definition of "clean" is not absolute, but depends on the individual steel production process and its in-service use of the final product. The term "clean steel" is therefore variable depending on the steel supplier and steel application. Due to the variable nature of the term "clean steel", Alan W. Cramb [3] proposes to talk more accurately of high purity steel as steel in the case of low levels of solutes (sulphur, phosphorus, nitrogen, oxygen and hydrogen) and low residual steel as steel with low level of impurities (copper, lead, zinc, nickel, chromium to name just a few) mostly originated from scrap.

Clean steels are steels with a low frequency of product defects that can be correlated to oxide inclusions. In addition, clean steel is increasingly understood as steel for which the composition is under tight control of alloying elements to improve product properties and property consistency. There is one constant in producing high purity, low residual and clean steel, which is the continual drive to reduce solute elements and residuals in all steels and control frequency, distribution and size of inclusions. Several studies on determining inclusion size and their frequency in the past resulted in rather similar numbers as shown in Figure 2.

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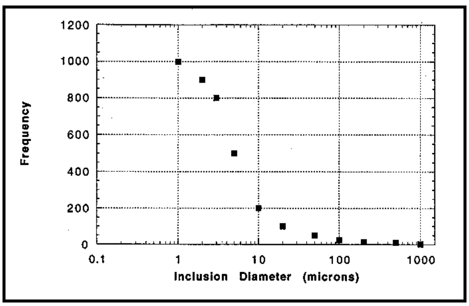

Figure 2. Frequency distribution of inclusion vs. inclusion diameter [4].

This figure explains quite clearly the problem of cleanliness assessment. There are only very few larger (macro) inclusions, that are difficult to detect for the reason that their number is small. In contrast, the number of very small (micro) inclusions is almost infinitesimal and their size makes them nearly undetectable. It appears that 5 microns (0.005 mm) represents the borderline between tolerable micro inclusions and potentially harmful macro inclusions. These sporadic large inclusions represent the foremost quality problem for steel plants in producing clean steel.

This paper highlights some metallurgical topics in producing clean steel and defines such steel as follows. Clean steels are those steels in which the frequency of oxide inclusions does not exhibit an adverse effect on manufacturing performance or final product behavior. There are no essential changes in the oxide cleanliness during the actual casting process. The start of casting during filling of the tundish and the molten steel turbulence during a ladle change represents the two critical phases in the casting process [5].

Clean steel technology based on slag free tapping and excellent de-oxidation practice also allows tight chemical composition control of alloying elements by improving the recovery of alloying elements. By applying this technology, demanding steel products can be produced to satisfy end users requirements in regard to properties and homogeneity. Furthermore, it results in an excellent yield and consequently improves the steel makers overall economical situation.

Modern High-Strength Low-Alloy (HSLA) provides the possibility to produce high strength steel with a relatively low alloying content. These steels are characterized by low carbon content and additions of micro alloying elements, i.e. niobium (Nb), vanadium (V), and titanium (Ti) to form microalloy carbides, nitrides, and/or carbonitrides. On the other hand, all micro alloying elements also show more or less strong affinity to oxygen and form stable but unwanted oxides, which can diminish the yield of those costly alloying elements.

The decrease in titanium yield with increasing slag carry-over from the furnace to the steel ladle is well known to all steel makers. Figure 3 shows the importance of the oxygen content in both, the steel and in the slag for alloying with titanium. A corresponding graph for niobium was not on hand, but it can be assumed that niobium follows the same systematic relationship, though the affinity of niobium to oxygen is much less as compared to titanium.

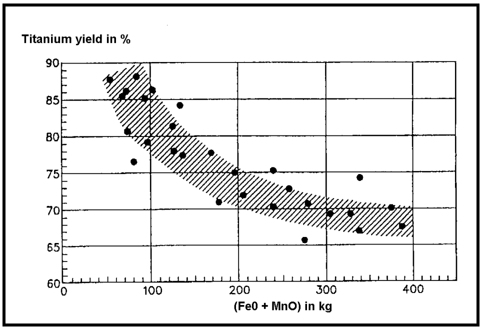

Figure 3. Titanium yield as function of ladle slag Oxygen content [6].

If both, steel and slag are properly deoxidized with Σ(FeO+MnO) in slag less than about one percent, the steel plant is awarded with a very economical recovery rate of niobium in the area of 98 percent. Because of the outstanding influence of niobium on the steel properties, a narrow scatter band of the niobium content in the steel is desired to guarantee the consistency of mechanical properties in the finished products.

However, due to its high melting point, Niobium does not melt in steel but goes into solution (7). This time consuming process must be taken into account when alloying adjustments are necessary to meet the final analysis.

Market Development for Modern Structural Steel Grades and Implication on Mill Engineering, Rolling Technology and Alloy Design

The requirements of the increasingly competitive heavy plate market necessitate an unending development of new plate steels. With both yield and tensile strengths increasing, Charpy toughness values increase with a simultaneously decrease of the toughness transition temperature while other material properties require constant improvement. The development that came exceedingly apparent starting around the turn of the century targeted not only in the direction of higher grades, but also in heavier plate gauges. At the same time the market of heavy structural plate surged (Figure 4).

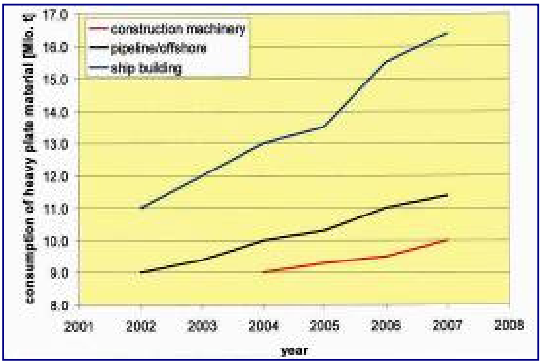

Figure 4. Reduction of plate thickness by using HSLA steel grades (base S355) [8].

Materials for medium-thick high-pressure gas transmission on-shore pipelines in grades up to X100/120 are developed and are subject to field test. For offshore deep-sea projects line pipe material up to about 50 mm are under investigation, Figure 5.

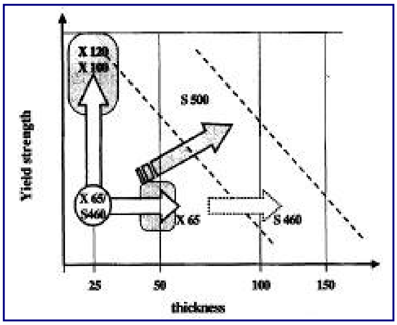

Figure 5. Process development trend [9].

For construction materials with 500 MPa minimum yield strength are produced in thicknesses up to 80 mm. Plates with 460 MPa SMY are available in gauges above 100 mm.

At the end of last century, the market for new plate mill equipment was quite poor. Just in time for the increasing market demand at the turn of the century, a new generation of powerful plate mills emerged and was equipped with a new piece of equipment - roll shifting (Figure 6).

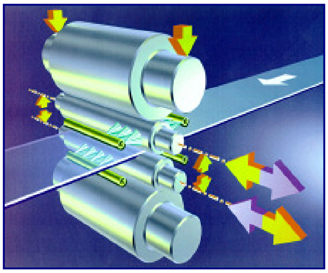

Figure 6. Work roll bending/shifting system (CVC plus®) [10].

The other most important advantage of this technological device is the application of higher roll forces and bigger moments of inertia, especially important in rolling heavy gauge plate in the thermo-mechanical rolling mode. The overall plate quality is improved in terms of flatness, profile and thickness, especially for critical borderline plate dimension, e.g. thin-gage materials. Last but not least, less passes are required resulting in 10 to 15 percent increase in overall productivity.

Most of the many brand-new heavy plate mills that are in the order books of mechanical engineering companies or under construction worldwide right now are equipped with roll shifting.

The Search for Crack-Free Slab Surfaces - Mechanical Properties of Steel at Elevated Temperatures

Cracks form when the tensile strain locally exceeds the yield strength of the steel. An understanding of the formation mechanism of different crack types caused by either thermal or mechanical strain requires comprehension of how tensile strains are generated in the solidifying shell and what the zones of low ductility are, in which the steel is most susceptible to cracking.

In continuous casting, defects are originated during the phase transformation from liquid to solid and during microstructural changes. Defects can occur both inside the slab and on the slab surfaces. Therefore, the cast structure is the one fundamental to slab quality.

Starting from the mold down the continuous caster, the stand shell is subject to numerous loads:

- Friction between the strand shell and the mold
- Strand rolls and segment transitions misalignments
- Ferrostatic pressure causing bulging
- Bending and straightening forces
- Phase transformation and micro structural transformation stress
- Thermal stresses

The temperature distribution ranges from the solidification temperature of about 1500°C in the mold down to almost 700°C at the torch-cutting machine. Even during stable casting operations, the occurrence of surface defects is largely influenced by the machine design, the casting and maintenance operations, and the steel grade.

In the following, the influence of the steel's chemical composition on the development of surface cracking will be discussed briefly with focus on High-Strength Low-Alloy (HSLA) steel grades that are characterized by low carbon content and the addition of microalloying elements.

Influence of the Carbon Content on Surface Defects

The influence of peritectic carbon content on the surface cracking susceptibility of low alloy steel grades is well known (Figure 7).

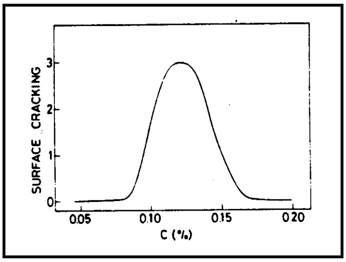

Figure 7. Effect of the Carbon in low-alloyed steel on surface cracking (schematic) [11].

It is shown that this phenomenon must be discussed in relation to the microstructural change during solidification and subsequent cooling. The austenite (γ) grain size significantly varies with the carbon content. As illustrated in Figure 8, the maximum grain size is found in about 0.09 to 0.16 percent of carbon (Figure 8a) due to the higher austenite formation temperature in this carbon region.

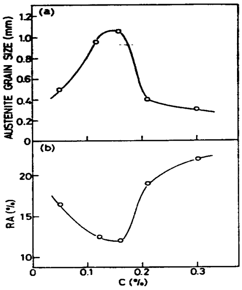

Figure 8(a,b). Effect of carbon on austenite grain size and calculated ductility (RA) [11].

The lower graph of Figure 8b shows the corresponding ductility values measured in reduction of area (RA).

The growth of the solidifying shell is not uniform and is also dependent on the carbon content. Another influence on the primary solidification structure and the secondary austenite grain size is the cooling rate. One of the most important elements in continuous casting in regard to solidification and crack formation is the mold. The mold's intensive heat removal directly effects shell growth to allow passing into the roll containment without rupturing. A lubricant (the casting flux) made of mineral materials helps to decrease friction between mold and the solidifying steel shell.

In the mold, axial stresses are set up in the shell owing to the friction between the oscillating mold surface and the shell surface. These stresses are tensile when the mold moves upwards relative to the shell and compressive when the relative motion of the mold is downwards (negative strip).

The mechanism of heat transfer from the strand surface to the cooling water is very complex. As shown in Figure 9 the most important part in this system is the gap between the strand shell and the mold surface.

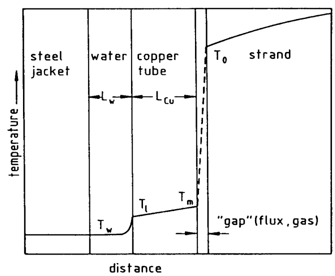

Figure 9. Temperature evolution between strand surface and cooling water [12].

Only perfect steady contact between strand shell and mold faces results in uniform heat extraction and homogeneous micro structural development.

The combination of the presented results of steel with different carbon ranges is summarized in Figure 10. The influence of the different carbon content on the development of the microstructure is obvious. In case of peritectic carbon contents (Figure 7 b) the steel not only forms coarser austenite grains, but is prone to form indentation or local wrinkle thus retarding heat extraction. Such local delay of cooling will increase the austenite grain even further, escalating the surface cracking susceptibility.

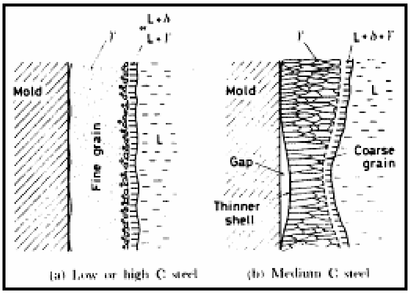

Figure 10. Austenite structure (schematic) of steel grades with different carbon content [11].

The main target is to optimize the chemical analysis concerning the carbon content and get around the crack susceptibility. Avoiding this critical carbon range of 0.09 to 0.16 percent and aiming for less than 0.09% carbon is preferred. A welcome side effect results from an increased toughness level of the material.

Influence of the micro-alloying elements on surface defects

Microalloyed steel grades distinguish themselves by reduced carbon content and the addition of microalloying elements, i.e. niobium, vanadium and titanium. Very early in the development of continuous casting, steel makers realized that HSLA steel grades showed a higher susceptibility to surface cracking on the products' surface and in particular at the cast products' corners compared to non-alloyed steels. Figure 11 illustrates the intensity of transverse surface cracking depending on different basic steel compositions.

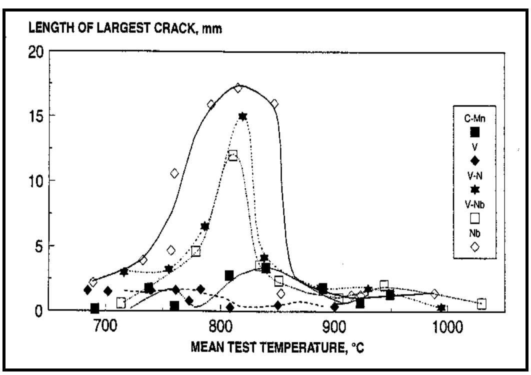

Figure 11. Variation of crack length with steel type and test temperature [13].

Whereas plain carbon-manganese steel grades put only very short cracks on view and do not vary with temperature, micro alloyed steels may distinguish themselves as crack-sensitive for possible transverse surface cracking. The crack initiation, preferable on deep oscillation marks, and their propagation along austenite grain boundaries is a manifestation of low hot-ductility of the steel at elevated temperatures.

The lower the ductility is, then the higher the material's crack susceptibility. The following Figure 12 depicts the ductility of a typical HSLA structural steel grade as function of deformation temperature.

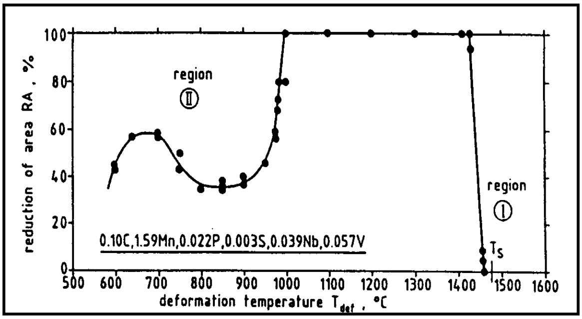

Figure 12. Typical example for HSLA ductility-temperature curve [14].

The graph shows two varying areas of low ductility:

- Area I – just below solidus temperature, steel shows no ductility at all. Cracks are mainly connected with columnar dendritic primary structure. This so-called zero-ductility accounts for internal cracking and is caused by liquid film formation from sulphur and phosphorus segregation to interdendritic liquid.

- Area II – this high temperature ductility area is the common problem by generating transverse cracking during bending and unbending and at the product corners. The causes for this ductility loss are many and the problem requires a more detailed look.

The investigation of crack sensitivity with careful consideration of the steel microstructure revealed that the high temperature ductility trough needed subdividing into two brittle temperature ranges. M.M. Wolf's distinction between an intermediate-temperature ductility trough (I) and a low-temperature ductility zone (II) is shown in Figure 13.

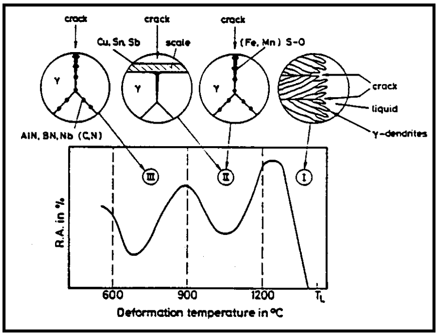

Figure 13. Low ductility (brittle) temperature ranges in the hot tensile test (schematic) [15].

As already stated, starting from solidification temperature the ductility remains zero until the interdendritic liquid freezes. Increasing RA values indicate the transition from brittle to ductile behavior.

- With descending temperature, an intermediate temperature ductility trough (Area II) opens at about 1200° C and continues down to 900°C. Due to the limited solubility of sulfur in the austenite at this temperature, fine (Fe,Mn)S precipitates along the austenite grain boundaries. The easy remedy is to lower the Sulfur content and especially in low-manganese steel grades to increase the Mn/S ratio to form less harmful manganese sulfides (MnS).

- The other mechanism of developing surface cracks in connection with residual elements such as Cu, As or Zn is of minor importance in continuous casting, but a recognized problem in hot rolling based on scrap-based steel making, copper penetration cracking, due to subscale enrichment of residuals.

- Soon after the ductility has almost recovered at a temperature of 900°C, a second low-temperature ductility trough opens down to about 700° C. The surfaces of specimens fractured in this temperature zone of reduced ductility exhibit precipitates of varying types of nitride inclusions. Common to all these nitride inclusions are their location at the austenite grain boundaries, particularly with large grain sizes.

While embrittlement in those temperature ranges does not occur in pure iron, it has been found in both plain carbon steel and especially microalloyed steel grades. This clearly indicates that embrittlement is not possible without some precipitates. Consequently, steel composition is extremely important in determining this area of reduced ductility.

The relationship between niobium concentration and reduction in area for a 0.18%C steel is illustrated in Figure 14.

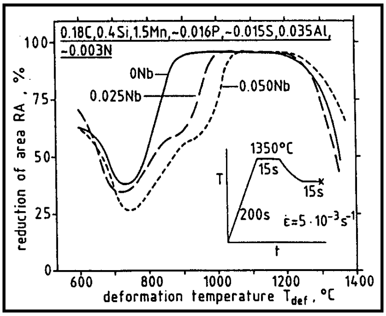

Figure 14. Effect of niobium on hot ductility in Al containing steel [16].

In this case, increasing Nb-content affects the ductility moving to higher deformation temperatures and widens the ductility trough. Knowing that nitride precipitates are largely responsible for lowering ductility, it is not surprising that decreasing nitrogen contents may have a beneficial influence on the problem. The influence of higher nitrogen levels on the ductility is deleterious on some important low temperature properties of steel strength and toughness. Accordingly, it is quite helpful to lower the nitrogen levels to technically and economically feasible values of about 50 ppm.

The final nitride former, titanium, is unique in being an element that is beneficial in minimizing the ductility problem. Figure 15 shows in the upper part (a) the effect of reducing nitrogen and, in the lower part (b), the influence of some titanium on the ductility.

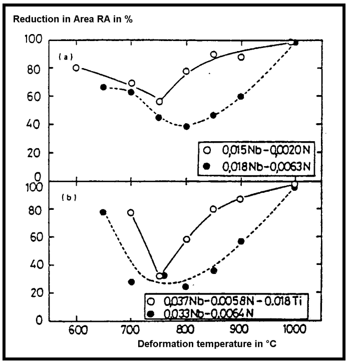

Figure 15. Influence of Nitrogen reduction or forming TiN on ductility [17].

A successful alternative to reduce the nitrogen content to the required low level, is adding stoichiometric amounts of titanium to form very stable titanium nitrides (TiN). Due to its lower solubility, TiN precipitates at high temperatures, leaving less nitrogen for the subsequent precipitation of potentially more detrimental nitrides.

Concerning nitrides and forming a circle back to the metallurgy of clean steel production, the other nitride forming element is Aluminum. As Figure 16 demonstrates quite clearly, increasing aluminum also causes a marked drop in ductility, particularly below 900°C.

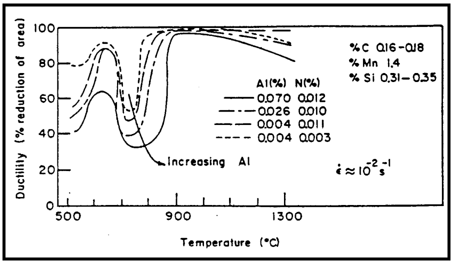

Figure 16. Influence of Aluminum on the hot ductility of steel [18].

Minimizing both aluminum and nitrogen narrows the ductility trough and results in much less drop of ductility. Again, the significance of steel making and ladle metallurgy is obvious in minimizing ductility trough issues.

Modern Continuous Casting Technology

The steel industry experienced transverse surface cracking of peritectic steel grades and HSLA steel grades during the development of continuous casting. In the early days of continuous casting, quality-conscious steel plants would scarf all HSLA slab surfaces and edges by machines and/or hand.

Figure 17. Typical transverse cracking.

Figure 17 displays edge cracking that is quite frequently found in casting microalloyed HSLA steel grades. Those defects are not visible on the as-cast slab surface. It is standard procedure to test scarf certain slabs of each casting sequence and strand manually and inspect for cracks. This practice ensures that all slabs delivered to the plate mill are free of defects. That is the only solution to avoid so called “zigzag cracks” as shown in Figure 18.

Figure 18. Zigzag cracks along the plate edge.

Those formerly transverse cracks at the slab surface develop into the typical Z-shape due to transverse and longitudinal plate rolling.

With a plate market that turned increasingly to the production of microalloyed low carbon steel grades, mechanical engineering designs attempted to address this grade specific issue of that alloy design in the engineering drawing plans of new continuous casting machines (Figure 19).

Figure 19. Ductility in the bending and straightening zone of CCM [19].

For each caster the material ductility is calculated for the full metallurgical length of the casting machine. As shown, the bending and straitening sectors are located at the maximum ductility values.

Another technology to avoid overcooling of the slab edges is to deactivate nozzle columns depending on the cast slab width (Figure 20).

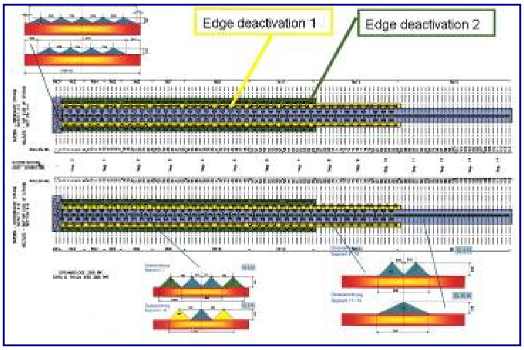

Figure 20. Deactivation of nozzle columns in a CCM [20].

Despite the progress made in CC design and process technology, the occurance of surface defects in the final product can still not be precluded totally. Though engineering companies do their best to design and develop casters capable to produce defect-free products, it is up the the steel maker and their maintenance operations to preserve excellent caster condition and appropriate steelmaking and caster operation.

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