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CLEAN STEEL TECHNOLOGY - FUNDAMENTAL TO THE DEVELOPMENT OF HIGH PERFORMANCE STEELS

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ABSTRACT: The use of clean steel technology (low sulfur with calcium treatment for inclusion shape control) is a fundamental building block in the development of high performance plate steels. A brief review will be presented of the benefits of calcium treatment and its effect on non-metallic inclusions (sulfides and oxides) and reducing sulfur levels. During the past thirty years the requirements for low sulfur levels have been reduced from 0.010% maximum to 0.001% maximum. The effects of clean steel practices on specific properties will be reviewed including tensile ductility, Charpy V-notch and fracture toughness, fatigue crack propagation and hydrogen-induced-cracking resistance. Traditional low sulfur plate steel applications have included pressure vessels, offshore platforms, plastic injection molds and line-pipe skelp. More recent applications will be discussed including bridge steels, high strength structural steels to 130 ksi (897 MPa) minimum yield strength, 9% nickel steels for cryogenic applications, and military armor.

KEYWORDS: clean steel, low sulfur, inclusions, toughness, fatigue, steel properties

Over the last three decades, the cleanliness of structural steels has been improved enormously. The challenge to improve cleanliness has been presented by a variety of applications which have required improvement in mechanical and other properties. The level of sulfur has been the principal focus to improving the cleanliness and thus the performance of steels. In the 1970's, 0.010% maximum sulfur was felt to be clean plate steel. Today, 0.001% maximum sulfur level is required for an increasing number of applications.

There has been a significant amount of effort in inclusion control over the past 30 years. Lamellar tearing problems in welded structures in the 1960's was a major initial factor in demanding cleaner plate steels. This also resulted in a better

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understanding of the influence of nonmetallic inclusions on steel performance. Furthermore, the benefits of low sulfur and low inclusion contents were found to improve toughness, ductility and fatigue properties of steels and thus the resistance to failure in service. These improved performing steels are being utilized in a wide range of applications. Most often it is the applications that have pushed the steelmaking improvements towards cleaner steels.

Steel Inclusions

When inclusion control in steels is considered, the primary concerns are indigenous non-metallic inclusions, which precipitate as discrete phases during the solidification of molten steel, e.g., sulfides and oxides. These inclusions are influenced by the steelmaking techniques that are used in the steelmaker's melt shop, as well as other processing that is subsequently used. Some of these influences will be discussed in the following text. Although oxides and sulfides are of particular interest in steel, other inclusions can also play an important role. In steels that are not aluminum killed, silicates are an important concern. Also when nitride forming elements are used in alloying, there can be a significant influence of nitride inclusions. For purposes of this review, only aluminum killed steels will be considered and the importance of controlling aluminum oxide and manganese sulfide inclusions will be emphasized.

Characterizing these inclusions is an important part of identifying the influences of different steelmaking practices. Various metallographic methods have been used in these characterizations. Quantifying the inclusion content differences between steels is also of concern. Identifying the influence of these inclusions upon mechanical and other properties is also of interest.

The non-metallic inclusions in plate steel are significantly influenced by the steelmaking processes that are used. This is particularly the case with sulfide inclusions. Our experience has been related to electric arc furnace (EAF) produced steels and, therefore, the discussion will be directed toward this particular operation. In EAF steelmaking, the sulfur levels can be reduced through double slag practices and until approximately 20 years ago this was the primary method used to achieve the lowest sulfur levels for structural steels. With the development of ladle metallurgy practices, sulfur levels could be reduced outside the EAF through various techniques. One of the most popular methods that has been used is calcium treatment (CaT). It is possible to achieve very low sulfur steels (maximum sulfur levels as low as 0.001%S) in conjunction with other desulfurization techniques within or outside the EAF using CaT.

After molten steel has been refined through a ladle metallurgy station, it is teemed into ingots or cast using continuous casting processes. Both casting processes influence the inclusion content in the final product. In ingot casting, due to the long solidification period, there can be segregation of sulfur at the top of ingot and near the centerline. However, with lower sulfur steels, there is less of a concern for this problem. In continuous cast slabs, there can be problems with reoxidation inclusions collecting near the top quarterline of the slab. Through use of various argon shrouding techniques, reoxidation inclusions are minimized in both casting methods.

Calcium Treatment

The primary emphasis of this paper is on calcium treatment of plate steels. We have a great deal of experience using this practice over the past 20 years. Because calcium has a boiling point below steelmaking temperatures, it has been found important to use a powder injection or wire feeding method to add calcium compounds to the molten steel. Both processes involve adding calcium compounds to the bottom of the ladle and stirring the bath with argon. Calcium has a very strong affinity for both sulfur and oxygen and therefore the benefits of both lower sulfur and oxygen content are achievable. The recognition that calcium has some limited solubility in molten steel was the key discovery, which led to the use of calcium treatment of production steels [1]. With some calcium in liquid solution, the chemical reactions with sulfur and oxygen can be performed more efficiently, removing them from the molten steel, with the sulfide and oxide phases being absorbed by the slag cover.

The effectiveness of a calcium treatment may be influenced by a number of parameters. For example, these may include the amount and chemistry of the calcium compounds, effectiveness of deoxidation prior to treatment, various injection and stirring parameters, molten steel temperature and chemistry, tapping practices, ladle refractory composition, teeming and casting practices. Any of these may have an influence on the efficiency of calcium treatment and thus on the inclusion structure of the calcium treated steel.

The benefits of calcium treatment are best described through reviewing how manganese sulfides (MnS) and alumina inclusion clusters form in a steel [1]. In conventional steels, MnS inclusions have a low melting point and are among the last to precipitate in the solidifying steel and thus tend to accumulate in the interdendritic areas of the cast structure. By the addition of calcium, CaS phases form and rise out of the steel and are absorbed by the slag. The remaining calcium sulfide phases have melting points closer to those of steel and thus are more evenly distributed throughout the steel.

Alumina inclusion clusters form in conventional steels almost immediately after the addition of aluminum for deoxidation. These are very high melting point inclusions and they begin to rise in the molten steel, growing, contacting each other, and forming extensive three dimensional arrays. Upon calcium treatment, calcium combines with alumina inclusions in a fluxing reaction, which forms much lower melting point individual, liquid, complex inclusions, which rise more easily out of the molten steel. The more calcium present in the inclusion, the lower the melting point of the $CaO{\cdot}nAl_2O_3$ inclusions (Ca-aluminates) that will form. The composition of these calcium aluminates becomes a "telltale" signature of the efficiency of the calcium treatment practice.

The remaining inclusions in calcium treated steels tend to be duplex, calcium modified inclusions which resist deformation on hot rolling. The calcium modification of the sulfide phase makes them harder at hot rolling temperatures in comparison to the steel matrix. This is the basic building block for inclusion shape control. However, even more subtle differences can be detected in the inclusion structure of these steels; these are a direct result of the efficiency of calcium treatment.

Inclusion Shape Control

It is very important to have a number of techniques available to characterize the inclusion content and distribution in a steel. Each method can have a separate contribution and therefore improve the overall understanding of the inclusion structure. Light optical microscopy is still a very valuable tool for this evaluation. In fact, at times it is the most important. Figure 1 exhibits the typical inclusions in a conventional higher sulfur steel. MnS inclusions elongate both individually and as a cluster and are pancaked during the hot rolling process. The alumina inclusions do not individually deform, but the clusters do and further contribute to mechanical property reduction and anisotropy. Calcium treatment assists in lowering sulfur content and provides inclusion shape control and the removal of alumina inclusions as demonstrated in Figure 2. These enhancements can also be shown through use of fractographic evaluation of various mechanical test specimens from the sample steels.

Quantitative analysis of inclusions that are in a steel can be attempted through evaluation of mounted metallographic samples through use of manual techniques or using quantitative image analysis. The availability of microprobe analysis is also vital to understanding inclusions in steel. This is very important in identifying inclusions and provides important support in determining the efficiency of the steelmaking practice.

In studies of calcium treated steels, six classes of inclusions have been identified [2]. These are summarized in Figure 3. Although more than one class of inclusion is normally present in any particular steel, generally a trend is noted in an evaluation and it is very useful in establishing a semi-quantitative level of effectiveness of the calcium treatment process.

Through metallographic studies of the calcium treated steels, it has been established that the presence of elongated inclusions (Classes C, E or F) and clusters of inclusions (Class D and F) are indicators of a poorer level of calcium treatment and of inclusion shape control. The optimum inclusions, Classes A and B, have unique chemistry. Figure 4 demonstrates the bull's-eye appearance of Class B and the intermingled sulfide and aluminate phases of Class A. The Ca-aluminate in Class A inclusions tend to have the highest Ca content of any Ca modified inclusions [2]. The intermingled nature of the Class A indicates that the sulfide and aluminate phases solidified at the same time, while the Class B aluminate phase formed first and became the nucleus for the sulfide phase. The presence of magnesium is a result of pick-up from refractory systems.

In early studies of calcium treated steels, the measurement of calcium content was used as an important tool in indicating quality of the steel. However, calcium measurement is only detected if it is present in inclusions, since there is no calcium in solid solution in steel. Therefore, if there is a very high level of inclusions in the steels that are calcium treated, then the measured calcium level may be high. If methods are used whereby inclusion content in general is reduced, these could show a lower calcium content. Therefore, calcium level alone is not always a good measure of effectiveness of calcium treatment [2].

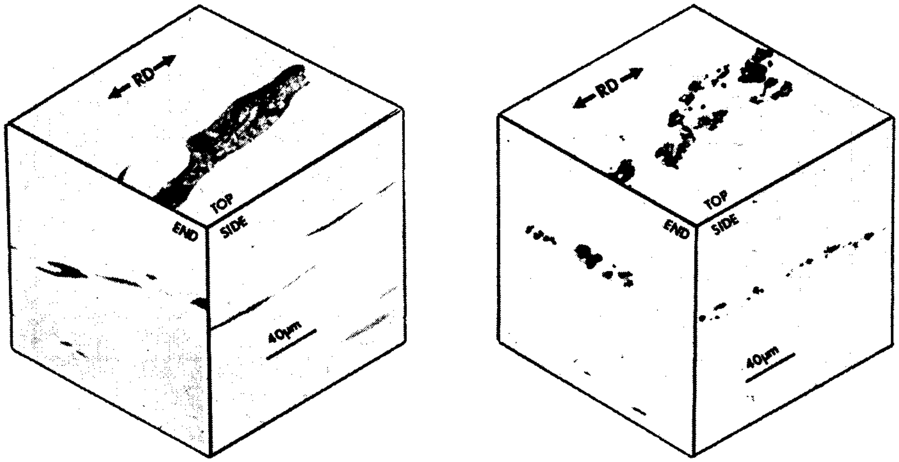

FIG. 1 -- *Composite of light photomicrographs showing Type II MnS inclusions (left) and Al_2O_3 inclusion clusters (right) in conventionally produced (CON) steel.*

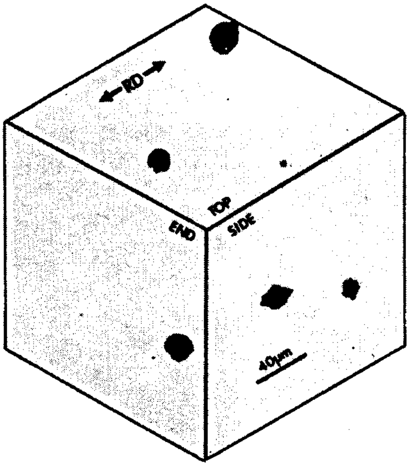

FIG. 2 -- *Composite of light photomicrographs displaying typical calcium modified inclusions in a CaT steel.*

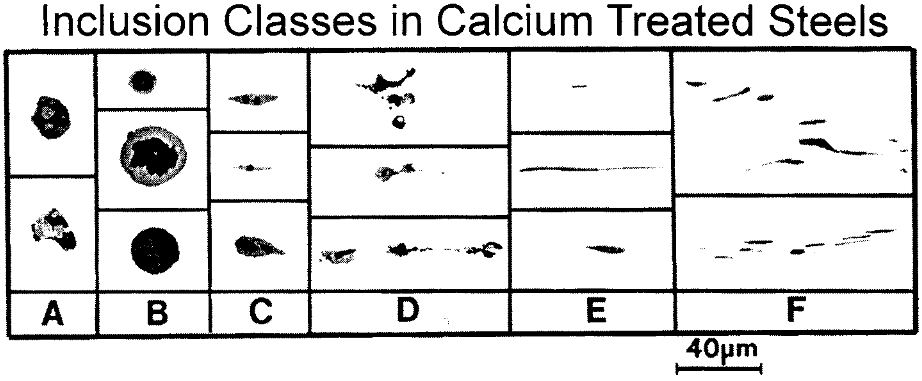

FIG. 3 -- *Six inclusion classes identified in calcium treated steels [2].*

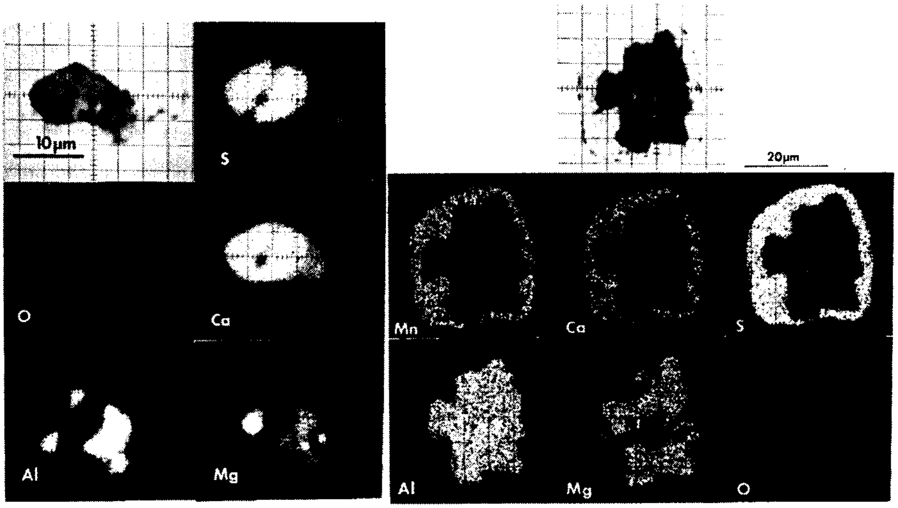

FIG. 4 -- *Energy dispersive x-ray maps of Class A and Class B inclusions displaying intermingled nature of Class A (left) and bull's-eye appearance of Class B (right).*

Effects on Mechanical Properties

Cleanliness and inclusion content can have a significant effect on mechanical properties depending on the property and the testing orientation. In any study of mechanical properties of steels with varying inclusion contents, it is very important to look at a number of testing orientations. Figure 5 provides the orientations that can be used. These orientations range from three testing orientations for tensile testing and up to six orientations for Charpy-V-notch (CVN) and fracture toughness, and fatigue crack growth rate testing. The effect of improved cleanliness on these properties is demonstrated in Figure 6. This figure summarizes the comparison testing of two A588, 3" (76 mm) thick plate steels, one conventionally produced (CON) with a 0.020% sulfur level and the other calcium treated (CaT) with a 0.003% sulfur level. Of particular note is the major differences in the through-thickness (S,ST,SL) testing orientations for all types of testing. The CaT steel also showed significantly improved upper shelf toughness in all testing orientations whether measured by CVN impact, dynamic tear (DT) or J-Integral elastic-plastic (J_{Ic}, T - tearing modulus) fracture mechanics tests. Fatigue crack propagation (FCP) threshold results require analysis for closure-correction to show the inclusion effects at very low crack growth rates. These results are discussed in more detail elsewhere [3].

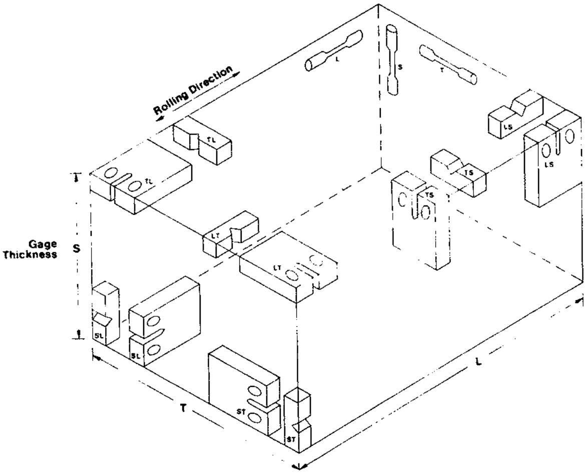

FIG. 5 -- *Schematic drawing showing the specimen orientations and designations per ASTM E399. Actual test location varies with test program.*

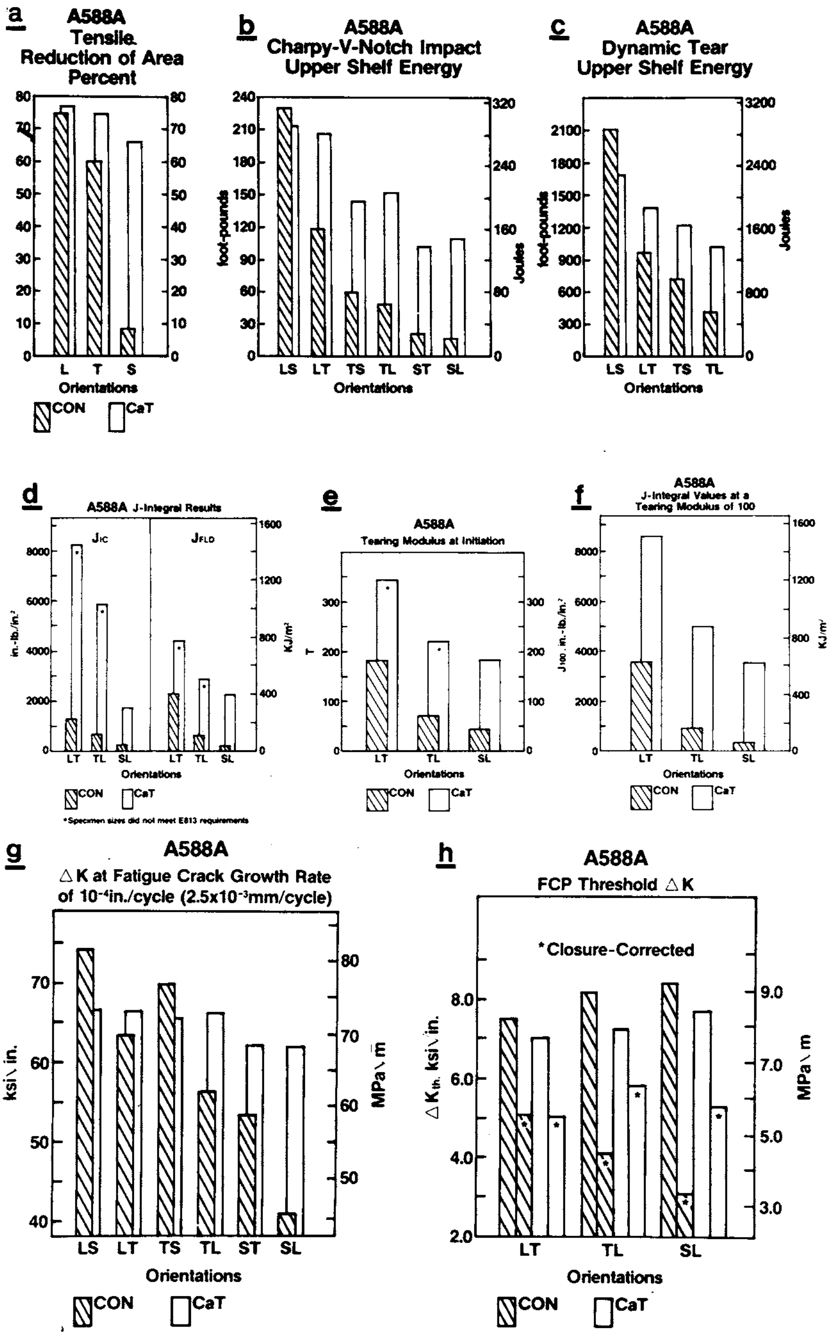

FIG. 6 -- *Summary bar graphs of comparison of CON and CaT Quality ASTM A588A.*

The higher inclusion content in the CON steel certainly influences the results shown in Figure 6. Of further importance is the clustering of the elongated and pancaked sulfide and oxide inclusions in the CON steel. Fractographic analysis of any of the tensile, toughness or FCP test specimens, particularly for the through-thickness orientations (S,ST,SL) dramatically reveals these clustered inclusions, as shown in Figure 7. The clustering of inclusions in clean steels can also lead to a degradation in properties. Figure 8 demonstrates this in hydrogen-induced-cracking (HIC) testing in A516 normalized, calcium treated carbon steel. HIC-testing involves exposing standard size samples to an acidic, hydrogen charging solution. Cracking initiates at inclusions and propagates along inclusion clusters [4].

Inclusion clusters can provide improvements in test results in certain orientations. For example, the LS orientation gave higher results for the CON steel in Figure 6 for CVN, DT and FCP tests because the elongated and pancaked clusters of inclusions act to blunt and deflect the cracking during the test.

High Performance Steels

In today's markets for steel plate there is a growing demand for improved steels to meet more challenging requirements. Clean steel practices have previously been required for lamellar tearing resistance for offshore platforms and machinery, improved toughness in line-pipe skelp and pressure vessels and better ultrasonic cleanliness in plastic injection molds. New high performance steels are being developed starting with very clean steel as the fundamental building block. A brief discussion of several examples is detailed in the following section. Table 1 gives the typical chemistries and minimum yield strengths of the steels to be discussed, as well as those referred to previously.

TABLE 1--*Example chemistries of steels discussed.*

ASTM Grade	C	Mn	Cu	Ni	Cr	Mo	Other	Y.S.
A588	0.15	1.11	0.29	0.19	0.59	0.05	0.06 V	50(345)
A516	0.22	0.92	0.08	0.05	0.06	0.01	...	38(262)
A709-HPS 70W	0.10	1.20	0.32	0.31	0.54	0.07	0.06 V	70(483)
A553	0.04	0.60	0.10	9.10	0.06	0.01	...	85(586)
A656-80	0.05	1.33	0.13	0.13	0.09	0.29	0.09 Cb	80(552)
LQ-130*	0.17	1.45	0.11	0.11	0.45	0.45	...	130(897)
HY-80*	0.16	0.31	0.12	3.12	1.57	0.54	...	80(552)

* LQ-130 - Bethlehem Lukens Plate grade in development
HY-80 - U.S.Navy specification MIL-S-16216

Y.S. - minimum yield strength, ksi (MPa)

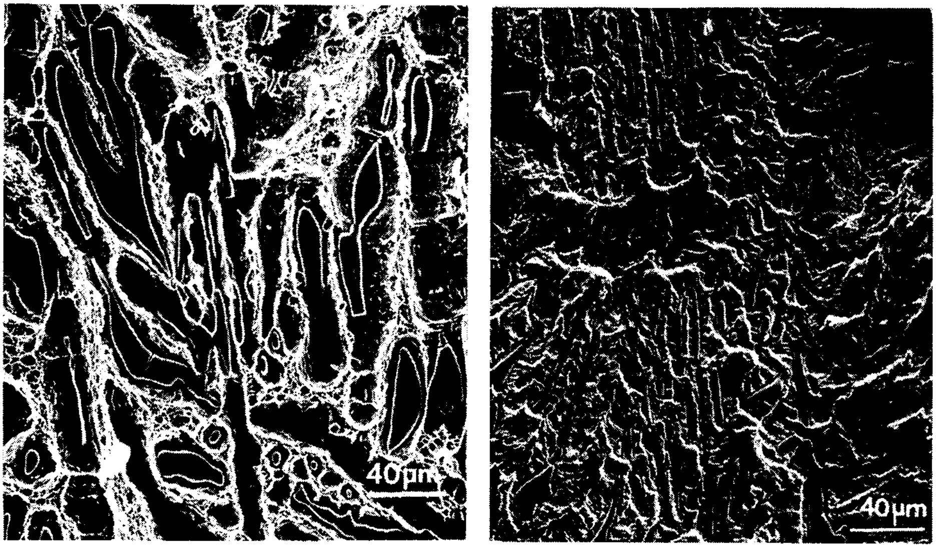

FIG. 7 -- *Scanning electron microscope fractographics exhibiting MnS inclusion clusters on SL oriented CVN specimen (left) and SL oriented FCP sample (right).*

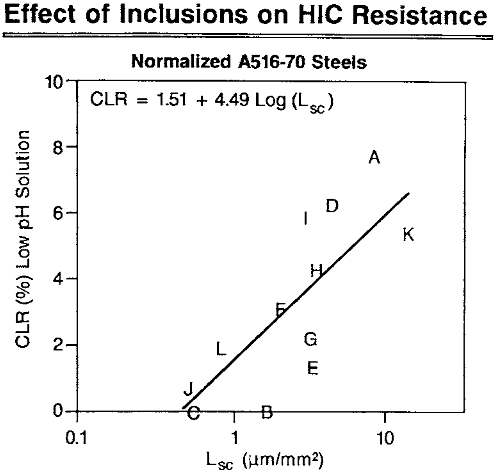

FIG. 8 -- *HIC resistance measured by crack length ratio (CLR) of normalized A516 related to inclusion stringer and cluster length factor L_{SC} determined metallographically for twelve plates.*

Bridge Steels

Traditional bridge steels are produced to ASTM A709, which has grades with yield strength level minimums of from 36 to 100 ksi (248-689 MPa). The toughness and welding practices for these steels have been based on the capabilities of these steels produced with 0.050% maximum sulfur levels and carbon contents at the higher ranges of mill experience. The Federal Highway Administration funded a research effort with the steel industry to develop high performance bridge steels with improved weldability and toughness. The result of this effort was a grade designated A709 HPS-70W with the nominal chemistry shown in Table 1 [5]. This quenched and tempered, weathering steel is produced with a sulfur level maximum of 0.005%. The carbon content has also been significantly reduced from a 0.17% maximum to 0.105% maximum. Bridges have been fabricated of this new grade and benefits in weldability realized. The improvements in the CVN toughness are summarized in Figure 9. These enhancements may make possible more aggressive design approaches in the future.

9% Nickel Steels for Cryogenic Vessels

Storage of liquified gases utilizes a variety of steels depending on the working temperature required. A553, 9% nickel steel is used at very low temperatures and is tested for CVN toughness at -320°F (-196° C). Over the past 20 years there has been continuing pressure to increase the required CVN toughness levels for improved design safety. This has required modifications to the melted chemistry. These changes and the resultant improvements in CVN impact properties are exhibited in Figure 10. Currently, sulfur maximum levels of 0.001% and low carbon and higher Ni levels are required for the most stringent CVN specifications.

High Strength As-rolled Steels

Steels used in the fabrication of construction and mining equipment have been increasing in strength to provide weight reduction and improved service performance. Traditionally higher strength levels required quenching and tempering (Q&T) heat treatments. However, advances in controlled-rolling technology have allowed development of steels to 80 ksi (552 MPa) minimum yield strength. ASTM A656 Grade 80 is the most popular plate steel grade for this application. Although A656-80 has a 0.035% maximum specified sulfur level, it has been traditionally been produced to 0.010% maximum sulfur to provide optimum toughness and lamellar tearing resistance. Lukens recently installed a Steckel mill, which produces plate in coiled form [6]. The nature of the coiled production route is that there is considerable rolling in one direction and thus a significant potential for developing property directionality. Thus, to provide the highest level of transverse CVN toughness, tighter controls on cleanliness are required. We are now producing this grade with 0.005% maximum sulfur. The results of this control are shown in Figure 11. The modest difference between longitudinal and transverse CVN results for a slab with a 24:1 reduction is a testament to the benefits of a lower sulfur level and inclusion shape control.

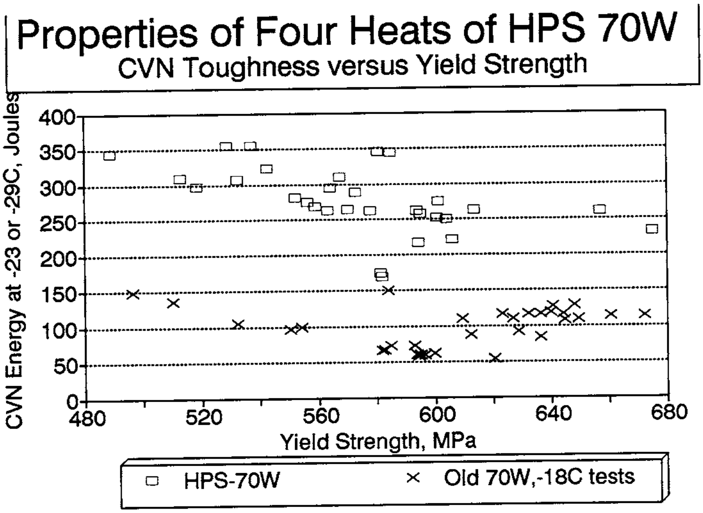

FIG. 9 -- *CVN data versus yield strength for ASTM A709-HPS 70W compared to traditional grade A709-70W.*

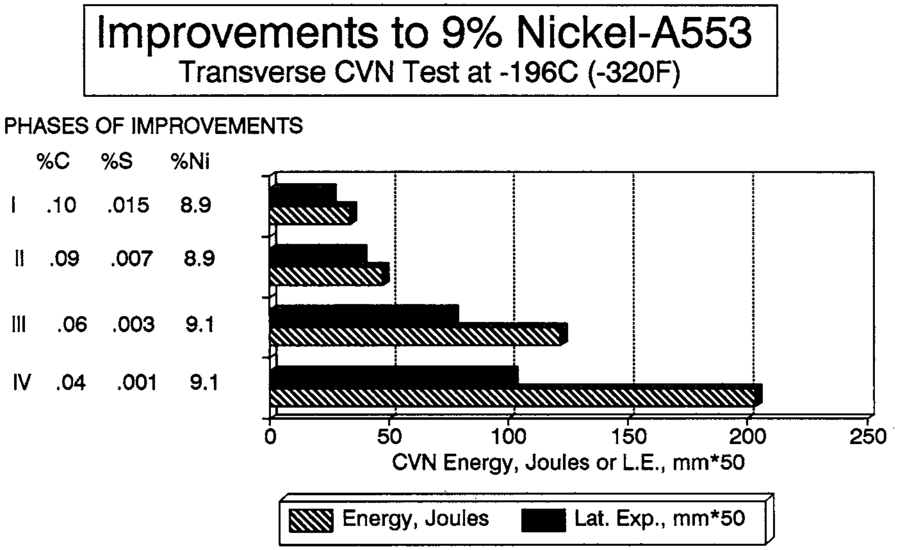

FIG. 10 -- *Improvements made to A553 steel and enhancements to CVN properties.*

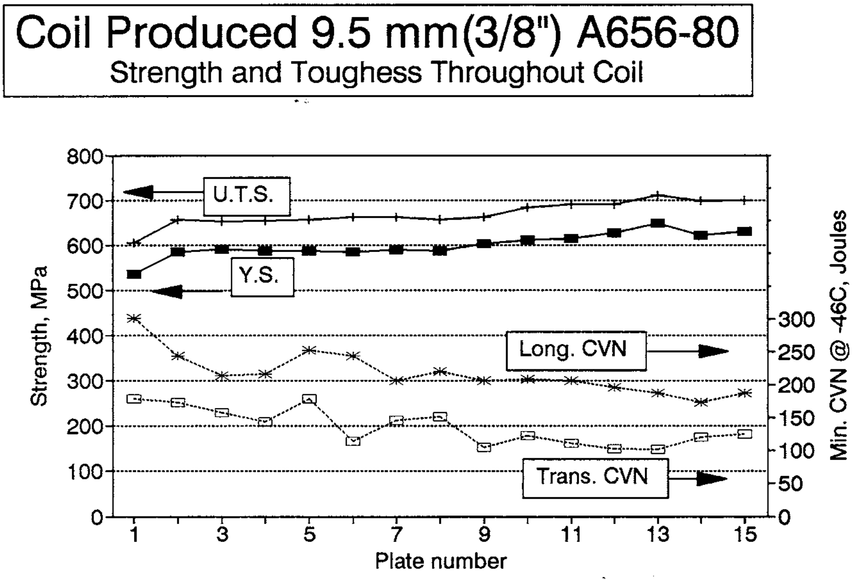

FIG. 11 -- *Strength and CVN results throughout coil of Steckel mill rolled A656-80.*

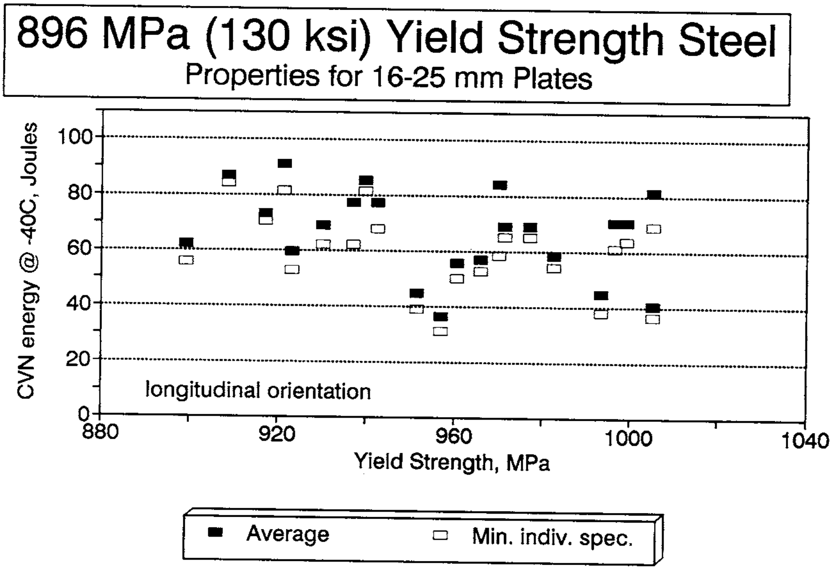

FIG. 12 -- *Summary of CVN and tensile data for Bethlehem Lukens Plate LQ-130 steel.*

Higher Strength Heat Treated Steels

With the increasing use of the A656-80 type steels there has been an accompanying demand for Q&T steels above the traditional 100 ksi (690 MPa) minimum yield strength level. Currently this demand has come for 130 ksi (896 MPa) minimum yield strength. Bethlehem Lukens Plate grade LQ-130 was developed for this application. To meet the CVN impact toughness requirements of equipment manufacturers, we have found it is necessary to produce this grade to a 0.001% maximum sulfur level. Figure 12 provides a summary of some of the latest results of this development.

U.S. Navy Armor Steels

The Navy specification for 80 ksi (552 Ma) minimum yield strength armor plate, MIL-S-16216 (HY-80), was developed in the 1950's for use on submarines. Specification requirements added over the years included CVN impact toughness testing at -120°F (-84 °C). However, the Navy was concerned whether the CVN test adequately represented the toughness behavior for applications where explosive events must be survived. The Naval Research Laboratory developed the dynamic tear test at -40 °F (-40 °C) as a more reliable quality control test for this challenging application. To meet this rigorous test, more control of the steelmaking process was required. Thus the latest specification requires a 0.008% maximum sulfur level with calcium treatment for inclusion shape control. The benefit of this change is displayed in Figure 13.

HIC-Tested A516 Steels

As discussed previously, normalized A516 steels for process vessels, in sour or hydrogen sulfide service require excellent cleanliness to pass specified HIC testing. This application continues to be one of the most demanding for clean steel production practices. Depending on requirements, either 0.002% or 0.001% maximum sulfur are dictated. The ability to consistently meet these levels is demonstrated by the distribution of sulfur levels shown in Figure 14 for the latest 100 heats produced for this application.

Summary

The preceding provided a review of the clean steel technology developed to allow the development of today's high performance steels. Low sulfur steels with inclusion shape control have been found to provide improved ductility, toughness, fatigue properties, as well as other behavior such as in HIC-testing. Today the need for these steels is required not only for special situations, but also for everyday structural applications such as bridges and construction equipment. We expect this demand will continue into the next century.

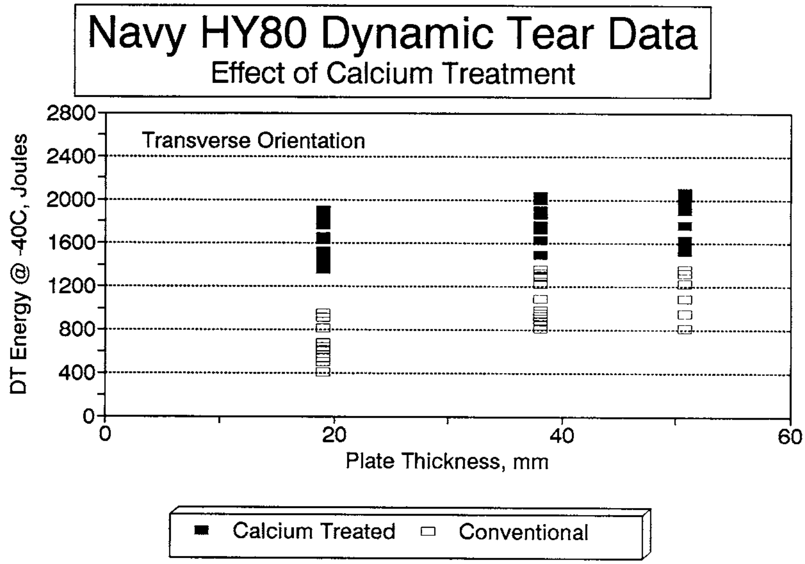

FIG. 13 -- *Benefits of using calcium treatment in HY-80 for improved DT results.*

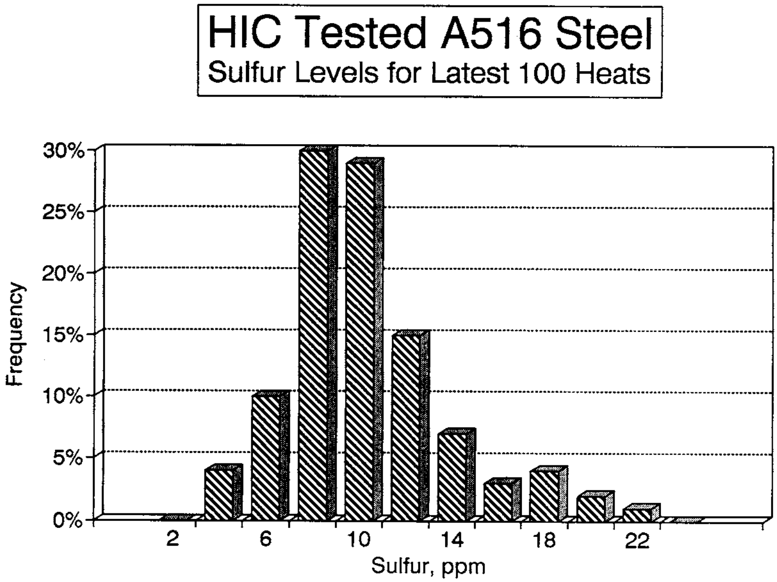

FIG. 14 -- *Distribution of sulfur levels for latest production of HIC-Tested A516. Testing according to latest ASTM standards.*

Acknowledgments

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