[illegible]

DOE F 241.3 (2-01) p. 2 of 2 ANNOUNCEMENT	UNITED STATES DEPARTMENT OF ENERGY (DOE) Scientific and Technical Information (STI) For Financial Assistance Recipients and Non-M&O/M&I Contractors	OMB Control No. 1910-1400
<div style="display: flex; justify-content: space-between;"> <div style="width: 48%; border: 1px solid black; padding: 5px;"> <p>PART II: STI PRODUCT MEDIA/FORMAT and LOCATION/TRANSMISSION (To be completed by Recipient/Contractor)</p> <p>A. Media/Format Information:</p> <p>1. MEDIUM OF STI PRODUCT IS: ☒ Electronic Document ☐ Computer medium ☐ Audiovisual material ☐ Paper ☐ No full-text</p> <p>2. SIZE OF STI PRODUCT <u>1.5 MB</u></p> <p>3. SPECIFY FILE FORMAT OF ELECTRONIC DOCUMENT BEING TRANSMITTED, INDICATE: ☐ SGML ☐ HTML ☐ XML ☒ PDF Normal ☐ PDF Image ☐ WP-Indicate Version (5.0 or greater) _____ Platform/operating system _____ ☐ MS-Indicate Version (5.0 or greater) _____ Platform/operating system _____ ☐ Postscript _____</p> <p>4. IF COMPUTER MEDIUM OR AUDIOVISUAL</p> <p> a. Quantity/type (specify) _____</p> <p> b. Machine compatibility (specify) _____</p> <p> c. Other information about product format a user needs to know: _____</p> </div> <div style="width: 48%; border: 1px solid black; padding: 5px;"> <p>PART III: STI PRODUCT REVIEW/RELEASE INFORMATION (To be completed by DOE)</p> <p>A. STI Product Reporting Requirement Review:</p> <p>☐ 1. THIS DELIVERABLE COMPLETES ALL REQUIRED DELIVERABLES FOR THIS AWARD</p> <p>☐ 2. THIS DELIVERABLE FULFILLS A TECHNICAL REPORTING REQUIREMENT, BUT SHOULD NOT BE DISSEMINATED BEYOND DOE.</p> <p>B. DOE Releasing Official</p> <p>☐ 1. I VERIFY THAT ALL NECESSARY REVIEWS HAVE BEEN COMPLETED AS DESCRIBED IN DOE G 241.1-1A, PART II, SECTION 3.0 AND THAT THE STI PRODUCT SHOULD BE RELEASED IN ACCORDANCE WITH THE INTELLECTUAL PROPERTY/DISTRIBUTION LIMITATION ABOVE.</p> <p>Released by (name) _____</p> <p>Date _____ (mm/dd/yyyy)</p> <p>E-mail _____</p> <p>Phone _____</p> </div> </div>		
<div style="border: 1px solid black; padding: 5px;"> <p>B. Transmission Information:</p> <p>STI PRODUCT IS BEING TRANSMITTED:</p> <p>☒ 1. Electronic via Elink</p> <p>☐ 2. Via mail or shipment to address indicated in award document (Paper products, CD-ROM, diskettes, videocassettes, et.) _____</p> <p>☐ 2a. Information product file name (of transmitted electronic format) _____</p> </div>		

Final Technical Report

Project Title: Development of the Automated Steel Cleanliness Analysis Tool (ASCAT)

Award Number: DE-FC36-99ID13820

Covering Period: September 24, 1999 through September 23, 2005

Date of Report: December 30, 2005

PI Gary Casuccio, (724) 387-1818, gcasuccio@rjlg.com

Recipient: RJ Lee Group, Inc.
350 Hochberg Rd
Monroeville, PA 15146

Subcontractors: Oak Ridge National Laboratory, RJ Fruehan Consulting, Aspex LLC.

Industry Partners: US Steel, MacSteel, J&L Specialty Steel, Bethlehem Steel, North Star Steel, LTV Steel, CSC Steel

DOE Contact: Debo Aichbhaumik, Project Manager - DOE Golden Field Office

Acknowledgment, Disclaimer and Proprietary Data Notice

Acknowledgment: "This report is based upon work supported by the U. S. Department of Energy under Award No. DE-FC36-99ID-13820".

Disclaimer: "Any findings, opinions, and conclusions or recommendations expressed in this report are those of the author(s) and do not necessarily reflect the views of the Department of Energy"

Table of Contents

Executive Summary	7
Introduction	9
Background	10
Technical Approach.....	12
Summary of Results	17
MACSTEEL	17
Steel Cleanliness	17
Castability	17
Spinel Formation	17
NorthStar Steel	18
LTV Steel.....	18
J & L Specialty Steel.....	18
U. S. Steel Intensive Study	18
Plant A	19
Castability Issues in Calcium Treated Grades	19
IF Degasser Grade Slag Conditioning Practice	19
Clogging and Quality Issues in Rephosphorized Grades	19
Behavior of Inclusions during Low Tundish Practices.....	20
TRIP (Transformation Induced Plasticity) High Al Steels.....	20
D&I Tin Grade Heel Trials.....	20
Tundish Flux Trials	20
Clogging in Motorlamination Grades	20
Effect of Inclusions on Motorlamination Grade Magnetic Properties	21
Plant B	21
Analysis of Clogging Behavior in Ti-containing Ultra-low Carbon Steels	21
Clogging in Si containing non-CaSi grades	21
Final Argon Plug Ladle Rinsing Effects on Inclusions (Ti-stabilized Ultra-Low Carbon Grades).....	21
ERW Hydrogen Induced Cracking (HIC) resistant steel practice development ..	21
Plant C	21
Degasser Final Circulation.....	21
Effect of Ar Purge on Inclusion Content during Initial Tundish Fill	22
Tundish Furniture Comparison	22
Tundish Flux Trials	22
Clogging in Degasser Si-containing Grades	22
Plant D	22
Tundish Furniture Trials.....	22
Al-based Slag Conditioning Trials.....	22
Assessment of CaSi Practices.....	23
Automotive Grade Low S Plugging	23
Plant E	23
Control of Tundish Slide Gate Erosion Behavior in Rounds Caster Grades	23
Tundish Change Joint Cutoff	23
Optimization of Environmental Cracking Resistance of Premium Seamless Pipe	23
Study of Practices to Mid-Wall Inclusion Defects in Seamless Pipe	23
Optimization of Degasser Usage on Pipe Grades	23

Accomplishments	24
Conclusions.....	25
Recommendations	26
References / Bibliography	28
Appendices	28

Table of Figures

Figure 1. ASCAT™ Inclusion Analysis System.	9
Figure 2. Inclusion characterization using the ASCAT™ Inclusion Analysis System.....	9
Figure 3. Example of supervised learning neural network.	14
Figure 4. Example of 3-D representation of the multi-dimensional inclusion clusters....	15
Figure 5. Comparison of three taxonomies for Ti-Al inclusions in steels	16
Figure 6. Visualization of the same three taxonomies shown in Figure 5 using pie charts to represent compositions of typical class members.	16
Figure 7. Process Flow Diagram Illustrating the Application of the ASCAT as a Production Tool and Laboratory Instrument.	26
Figure 8. Diagram illustrating potential Metals Cleanliness markets for the ASCAT	27

Executive Summary

In September 1999, RJ Lee Group, Inc. (RJLG) was awarded a contract from the US Department of Energy (DOE), through the Industries of the Future program, to develop technology to permit steelmakers to evaluate the quality of the steel through the analysis of individual inclusions. The project, entitled Development of the Automated Steel Cleanliness Analysis Tool (ASCAT™), was performed through a combined effort of RJLG, Dr. Richard Fruehan, Oak Ridge National Laboratory (ORNL), and several Industry Partners.

The ASCAT was developed around a next-generation computer controlled scanning electron microscopy (NG-CCSEM) platform and specialized analysis/interpretation software designed to relate inclusion characteristics to overall steel cleanliness, and other metallurgical issues associated with the steel making process. The objective was to develop technology to increase overall inclusion characterization information while minimizing individual sample analysis time to enable plant personnel to make adjustments in the steel making process to improve product quality and prevent problems such as nozzle clogging. In addition, ASCAT can be used as a research tool to improve the steel making process resulting in increased production and profits while saving energy.

During the course of the project, the ASCAT was tested in a variety of steel making applications. Working in conjunction with Industry Partners, samples were collected at various stages in the steel making processes to help understand the transformation of inclusion chemistries. Some of the projects that were investigated in this project included: nozzle clogging due to calcium aluminates or magnesium spinels; varying calcium additions to optimize castability; steel cleanliness versus casting time; comparison of inclusion content to standard analytical methods; hardware changes such as tundish linings and their overall effects. As a result of these and other studies, two papers were prepared with Industry Partners and presented at the Iron and Steel Society's 2003 Conference and Exposition in Nashville, TN. One of these papers, "Inclusion Analysis to Predict Casting Behavior" received the American Iron and Steel Institute (AISI) Medal for the publication with the most technical merit and was subsequently published in the September 2004 issue of Iron and Steel Technology.

In addition to projects performed with several Industry Partners, an Intensive Study was performed with U.S. Steel. During the Intensive Study, thousands of samples were analyzed to investigate numerous issues specific to several steel plants within US Steel. As a result of these trials, U.S. Steel was able to make process changes that resulted in significant cost and energy savings. Two additional papers have resulted from these investigations. One was presented at the AISTech 2004 conference and ultimately was published in the September 2005 issue of Iron and Steel Technology. The second paper will be presented at the AISTech 2006 conference in May of 2006.

During the course of this project, a number of the world's largest steel companies utilized the ASCAT technology and discovered that it enabled better overall management of the steel making process, resulted in production of higher quality steel, and increased production. Representatives of the steel industry have stated that the ASCAT is a "totally unique" system that provides great amounts of data allowing potential control of desired inclusions for product design; has been extremely helpful in improving the steel making progress; identifies the causes and predicts clogging of nozzles; and improves the incidence of downgraded products.

The ASCAT is being recognized as a valuable tool by the steel industry and investigation into competitive technologies conducted by ORNL concluded that the ASCAT will be clearly superior in performance and features than anything being presently tried by U.S. steel producers.

With respect to energy savings, the ASCAT greatest contribution will be related to reducing the

need to perform remelts. Direct energy savings of ASCAT assuming 100% market penetration with 0.5% remelt industry-wide would result in energy saving on the order of 3.2×10^{11} btu or 0.25% of steel industry energy consumption.

In summary, the ASCAT permits acquisition of inclusion size and composition data at a rate never before possible in SEM-based instruments. With built-in customized intelligent software, the data is automatically sorted into clusters representing different inclusion types to define the characteristics of a particular heat. In terms of performance, the ASCAT (1) allows for accurate classification of inclusions by chemistry and morphological parameters, (2) can characterize hundreds of inclusions within minutes, (3) is easy to use (does not require experts), (4) is robust, and (5) has excellent image quality for conventional SEM investigations (e.g., the ASCAT can be used as a dual use instrument).

Results of this study clearly indicated that the ASCAT will significantly advance the state-of-the-art in inclusion analysis in metal samples and addresses a broadly recognized need of the steel industry. Based on the success of this program, it is recommended that marketing and sales activities be initiated focusing initially on the laboratory version of the ASCAT. It is also recommended that efforts continue on the development of a production version of the ASCAT, and that the inclusion clustering software be integrated as part of the standard ASCAT product package.

Further, it is recommended that methods be developed to automatically apply problem-specific information into the ASCAT software to help select the optimum inclusion class partitions and to minimize direct intervention from experts.

With respect to commercialization, our steel partners are among the top integrated and SBQ (special bar quality) producers in the United States. They represent "early adopters" of ASCAT technology and will be the cornerstones to a solid marketing and sales strategy. By capitalizing on their experience, publications, and testimonials, we will be able to demonstrate concrete evidence of the value of ASCAT to prospective customers. The partner relationships that were cultivated during the Industries of the Future project will be invaluable to the ultimate success of the ASCAT.

Introduction

The objective of this study was to develop the Automated Steel Cleanliness Analysis Tool (ASCAT™) to permit steelmakers to evaluate the quality of the steel through the analysis of individual inclusions. By characterizing individual inclusions, determinations can be made as to the cleanliness of the steel. Understanding the complicating effects of inclusions in the steelmaking process and on the resulting properties of steel allows the steel producer to increase throughput, better control the process, reduce remelts, and improve the quality of the product.

The ASCAT (Figure 1) is a steel-smart inclusion analysis tool developed around a customized next-generation computer controlled scanning electron microscopy (NG-CCSEM) hardware platform that permits acquisition of inclusion size and composition data at a rate never before possible in SEM-based instruments. With built-in customized "intelligent" software, the inclusion data is automatically sorted into clusters representing different inclusion types to define the characteristics of a particular heat (Figure 2).

Figure 1. ASCAT Inclusion Analysis System.

The ASCAT pictured above is designed for laboratory/diagnostic applications. An environmentally-hardened version will be available for production applications.

Figure 2. Inclusion characterization using the ASCAT Inclusion Analysis System.
Inclusion characterization and identification can be accomplished in less than 1 second.

The ASCAT represents an innovative new tool for the collection of statistically meaningful data on inclusions, and provides a means of understanding the complicated effects of inclusions in the steel making process and on the resulting properties of steel. Research conducted by RJLG with AISI (American Iron and Steel Institute) and SMA (Steel Manufacturers of America) members indicates that the ASCAT has application in high-grade bar, sheet, plate, tin products, pipes, SBQ, tire cord, welding rod, and specialty steels and alloys where control of inclusions, whether natural or engineered, are crucial to their specification for a given end-use.

Example applications include castability of calcium treated steel; interstitial free (IF) degasser grade slag conditioning practice; tundish clogging and erosion minimization; degasser circulation and optimization; quality assessment/steel cleanliness; slab, billet or bloom disposition; and alloy development. Additional benefits of ASCAT include the identification of inclusions that tend to clog nozzles or interact with refractory materials. Several papers outlining the benefits of the ASCAT have been presented and published in the literature.^{1,2,3} The paper entitled *Inclusion Analysis to Predict Casting Behavior* was awarded the American Iron and Steel Institute (AISI) Medal in 2004 for special merit and importance to the steel industry.

The ASCAT represents a quantum leap in inclusion analysis and will allow steel producers to evaluate the quality of steel and implement appropriate process improvements. In terms of performance, the ASCAT (1) allows for accurate classification of inclusions by chemistry and morphological parameters, (2) can characterize hundreds of inclusions within minutes, (3) is easy to use (does not require experts), (4) is robust, and (5) has excellent image quality for conventional SEM investigations (e.g., the ASCAT can be utilized as a dual use instrument).

In summary, the ASCAT will significantly advance the tools of the industry and addresses an urgent and broadly recognized need of the steel industry. Commercialization of the ASCAT will focus on (1) a sales strategy that leverages our Industry Partners; (2) use of "technical selling" through papers and seminars; (3) leveraging RJ Lee Group's consulting services, and packaging of the product with a extensive consulting and training program; (4) partnering with established SEM distributors; (5) establishing relationships with professional organizations associated with the steel industry; and (6) an individualized plant by plant direct sales program.

Background

Characterization of inclusions is important because there is an increasing demand for cleaner steels with low inclusion (defect) content. Further, inclusions in the steel often must have defined properties (chemistries). The composition, and hence the properties, of the inclusions can be controlled through the chemistries of the metal and slag. By controlling the properties of the inclusions, higher quality steel can be made. However, despite the major advances in inclusion control, there has been no rapid and accurate method for determining the type, size and number of inclusions present in steel samples. Historically, a post-mortem analysis is performed on samples using manual SEM methods or conventional metallographic techniques long after the steel has been fully processed. Thus, the ability to make modifications to the process would typically require

¹ Story, S.R., Piccone, T.J., Fruehan, R.J., and Potter, M., "Inclusion Analysis to Predict Casting Behavior," Iron & Steel Technology, Sept. 2004, pp. 163-169.

² Ahlborg, K., Fruehan, R.J., Potter, M., Badger, S., and Casuccio, G., "Inclusions in Aluminum-Killed Steel with varying Calcium Additions," ISSTech 2003 Conference Proceedings, Vol. 2, pp. 177-194.

³ Story, S.R., Smith S.M., Fruehan, R.J., Casuccio, G.S Potter, M.S., and Lersch, T.L., "Application of Rapid Inclusion Identification and Analysis," Iron & Steel Technology, Sept. 2005, pp. 41-49.

scientific studies that were intensive in-terms of personnel and cost. Also, analysis and interpretation of a limited number of inclusions using manual techniques may not truly reflect the cleanliness or the type of inclusions present.

Inclusion analysis using metallographic (optical microscopy) procedures involving examination of visible inclusions on a polished surface can be used to assign measures of "cleanliness", referred to as JK ratings. Following established criteria and guidelines, inclusions are "grouped" into rather diffuse categories such as Types A, B, C and D, which correspond to four classes: oxides, silicates, sulfides, and globulars.^{4,5} The ratings are based on morphological similarities and not chemistry, and thus provide no information on the composition of the inclusions. With the numerous individual types of inclusions that could fall into each category, true inclusion characterization is not possible using this approach.

Optical emission spectroscopy, or "spark" analysis, is currently being use in the evaluation of steel. However, this analysis only provides a basic chemistry of the steel and not an in-depth analysis of the inclusions contained within the heat. Inclusions can, however, actually affect critical characteristics of a particular heat.

Ultrasonic testing methods are also currently employed. These techniques allow for analyzing large volumes of steel fairly quickly. The results can provide a macroview of the heat and the general characterization in terms of spatial distribution of the very large inclusions. However, the ultrasonic analysis also does not provide information on inclusion composition.

While each of the above techniques can provide useful information, they do not allow for a micro-chemical analysis of the steel. The need for chemistry data on individual inclusions was largely ignored due to lack of appropriate technology at the time the metallographic methods were being developed. However, there are an ever-increasing number of steel applications in which the number, size and distribution of inclusion types based on composition needs to be tightly controlled. CCSEM is the obvious technology on which to base such specific inclusion control. The use of CCSEM to characterize and assess inclusion type and mineralogy and relating these to both process variables and ultimate mechanical properties has been recognized by the steel industry since the late 1970's.^{6,7} However, a variety of factors have prevented CCSEM from developing into a widespread and standard industry tool including the downsizing of the domestic steel industry in the early 1980's, and the lack of appropriate computer-based technology to provide the needed information.

Interestingly the technology barrier had little to do with the knowledge of steelmaking. Instead, the technology issue was primarily related to (1) the lack of appropriate software; (2) the state of the art in electronic components and computer architecture and (3) the ability to intimately couple the analysis system to the SEM for both beam positioning and command set communication. SEM technology, like all other analytical technology employed in the production process, has evolved first as a research tool, then as a quality assurance and failure analysis tool, and now is ready to move to a process control tool.

⁴ ASTM E45-97 (2002) Standard Test Methods for Determining the Inclusion Content of Steel

⁵ ASTM E1122-96 (2002) Standard Practice for Obtaining JK Inclusion Ratings Using Automatic Image Analysis

⁶ Lee, R. J., Hsun Hu, "Automatic Image Analysis of MnS Precipitates in 3 Percent Silicon Steel", Published in United States Steel Research Laboratory Technical Report, December 1978.

⁷ Lee, R. J., W. A. Spitzig, J. F. Kelly, R. M. Fisher, "Quantitative Metallography by Computer-Controlled Scanning Electron Microscopy", Published in the Journal of Metals, Vol. 33, No. 3, pp 80, March 1981.

The conversion of the SEM from a research instrument to a production tool has only recently begun to take place. For example, during the past ten years, the SEM has been successfully re-cast as a critical-dimension measurement tool for use in the semiconductor industry. The critical-dimension SEM needed to be highly automated and much more reliable than their research counterparts. This was successfully accomplished by designing the SEM technology around a specific application. Today, critical-dimension SEMs are now found in every modern computer chip manufacturing facility in the world.

In summary, the ASCAT addresses a market need to monitor the effects of inclusions in the steelmaking process to allow steel producers to evaluate the quality of steel and implement appropriate process improvements, and represents the first focused effort to bring CCSEM technology as a standard component of the steel manufacturing process.

Technical Approach

Investigating the very small inclusions in steel, which are the building blocks of the large inclusions detected by other methods, requires the use of electron microscopy. Manual scanning electron microscopy (SEM) analysis combined with energy dispersive spectroscopy (EDS) has been used in the past, but this analysis approach is limited by the intensive nature involved, (i.e. an individual has to analyze individual inclusions which is very time consuming). And while this technique will fully characterize the inclusions, the time involved to analyze statistically valid numbers of inclusions is substantial. Automating the process of detecting and acquiring individual inclusion properties can make the SEM a powerful tool for analyzing steel heats. It can achieve this by increasing the number of inclusions analyzed from the tens or hundreds to the thousands while decreasing the total time involved from days and weeks to minutes. This ideology led to the development of the ASCAT.

To test the potential of the ASCAT to meet the objectives of the study, the project team worked with the Industry Partners to develop test projects to evaluate the ability of the ASCAT to meet industry needs. The experimental methodology consisted of a multiphase approach. The first phase consisted of initial studies to determine the optimal basic analysis, focusing on the quality of the inclusion data while sacrificing speed. This included establishing basic setup criteria (e.g., number of particles/analysis, elements of interest, time spent on each inclusions, size ranges of inclusions, etc.). After the analysis parameters had been established, re-analyses were performed to verify the reproducibility of the results.

The next phase involved optimizing the analysis without losing the quality of the data that was being produced. Studies were performed that involved major and minor modifications to both the hardware and software sides of the analysis. These modifications allowed for major decreases in time while maintaining (and sometimes increasing) the number of inclusions analyzed per unit time. Hardware changes were made so that more X-ray counts could be collected and analyzed in shorter amounts of time. What originally took multiple seconds in X-ray collection was reduced to less than one second during the course of this project. These improvements resulted in decreasing the overall time of analysis from over two hours to less than 30 minutes.

A key component of the project involved investigation of neural networks and statistical cluster analysis methods as alternative means of classifying inclusions as metallurgical phases. For many practical purposes and in the current implementation of ASCAT, assignment of inclusions to recognized metallurgical species can be done on the basis of chemical composition, or equivalently, based on the EDS peak counts. The initial and current implementation of ASCAT uses a set of logical rules to assign individual inclusion analyses to metallurgical entities. The logical rule sets have evolved from iterative evaluations by steel-inclusion experts and ASCAT data analysts. This

approach has been highly successful.

A salient observation from our ASCAT experience with steel-industry end-users is that the range of applications is much more extensive than originally expected, and the full range of applications has yet to be defined. To date the logical rule sets have proven to be remarkably robust with regard to application to new problem-domains; however, some adjustments with expert over-sight and intervention has been required. Therefore, in anticipation of a continuing need to re-create logical rule sets, or acceptable alternatives, and a desire to minimize turn-around-time and expert time commitments, a commitment was made to investigate alternative means to composition-based classification of ASCAT inclusion data sets.

An expert in neural network technology associated with ORNL, John D. Allen, led implementation and evaluation of two classification methodologies based on neural networks. Method discovery and initial demonstrations were implemented. The computer programs were implemented for discovery and demonstration purposes and were not developed nor documented to the point of independent functional entities.

One neural network investigation provided an evaluation of supervised learning. A neural network was implemented with adjustable parameters to facilitate examining the sensitivity of results to the network configuration. Composition information was derived from ASCAT EDS data sources in two manners: (i) from X-ray counts for peaks pre-selected during the configuration of the ASCAT analysis and (ii) from re-analysis of stored EDS spectra. The training data was provided in the form of assignments to metallurgical or compositional species, either manually by experts or through the application of logical rule sets. A sub-set of an inclusion ASCAT data was selected for training purposes. The trained neural network was then used to classify the remainder of the inclusion data set. The expert or logical rule assignments were compared with the neural net assignments. In general, good agreement was obtained once the network configuration had been tuned and the selection of inputs optimized.

The supervised learning evaluation highlighted the need to provide convenient and efficient means of generating assignments within the learning data set. A schematic of a successful supervised learning neural network is shown in Figure 3. The color and size coding indicates variations in the weighting of various nodes. The number of inputs (bottom row nodes) equals the number of elements used in the ASCAT analysis, and the number of outputs (top row nodes) equals the number of assigned metallurgical species.

Figure 3. Example of supervised learning neural network.

The number of inputs (bottom row nodes) equals the number of elements used in the ASCAT analysis and the number of outputs (top row nodes) equals the number of assigned inclusion classes.

To eliminate the need to develop training sets, an approach was proposed and investigated to use neural networks to discover clusters in unstructured inclusion data sets. A hybrid approach was used in which a symmetric, hourglass, neural network was first used to obtain a low-dimensional set of 'principal' components; then a density (clustering) filter was applied to the neural net principal components. In the first step, the network was configured such that the input and output nodes were equal in number to the number of EDS (element) inputs and the number of nodes in the middle layer was equal to the number of principal components. The network was trained until the outputs were equal to the inputs. The resultant values of the middle layer nodes comprised the input to the cluster filter. The hybrid method was very promising but suggested that more traditional statistical methods might also be effective.

Statistical methods for finding clusters in unstructured data have been reported and are well-documented. Two methods were investigated in detail for use with ASCAT inclusion data sets: ART2A and k-Means. ART2A has become a method of choice within the airborne particulate analysis community. To perform an ART2A cluster analysis, it is necessary to specify a goodness-of-fit for members within clusters. The ART2A algorithm then discovers the requisite number of clusters such that all analyses are within the specified distance of their cluster center. The k-Means method operates in almost an inverse fashion in that the desired number of clusters is specified and the best fitting cluster centers and memberships are calculated. Neither of these methods requires a training set; however, some basis must be provided for selecting the optimum number of clusters (i.e., the best taxonomy for the problem being investigated).

Figure 4. Example of 3-D representation of the multi-dimensional inclusion clusters.

A cluster analysis tool was implemented as a Windows program to facilitate performing cluster analyses with different methods and parameter selections and for efficiently reviewing and editing the resultant cluster memberships. The cluster analysis program was called ARTClass because of its genesis with the ART2A method and its ultimate objective of assigning inclusions to classes. ARTClass includes data preparation and pre-processing options for using data from conventional ASCAT data stores as well as from other compositional and morphological studies. ARTClass was also configured to automatically generate a variety of reports appropriate to ASCAT metallurgical investigations. Options were implemented to facilitate obtaining one or more taxonomies (analyses yielding different numbers of clusters) which could then be examined to determine the best grouping for the specific problem being investigated. ARTClass also contains means of developing and analyzing groupings based on direct expert calls and from the application of logical rule sets.

As noted, a common limitation of statistical methods is that an informed decision must be made regarding method parameters and the selection of the parameters ultimately determines the number of groups, or clusters, found within a data set. Means have been proposed for using statistical and information-content measures to determine the optimum number of clusters. However, in our experience these measures are not very robust for noisy data sets (such as a speed-optimized ASCAT analysis) and for intricate cluster groupings. Furthermore, often the preferred grouping for a particular metallurgical investigation may not be the same as the statistically optimum grouping. In order to facilitate evaluation and comparison of taxonomies, several visualization and interactive editing capabilities were implemented in ARTClass. Figure 5 and Figure 6 illustrate two visualization methods of comparing taxonomies and of assessing uniformity within a group and differences among groups. These two visualization presentations provide the platforms for interactive editing tools for combining or splitting groups and for re-assigning members on a case-by-case basis using drag-and-drop.

Figure 5. Comparison of three taxonomies for Ti-Al inclusions in steels
Illustrated are 4, 10, and 18 classes – using stacked bar graphs to represent the composition of class members.

Figure 6. Visualization of the same three taxonomies shown in Figure 5 using pie charts to represent compositions of typical class members.
In each vertical panel, each row represents a different class panel; the left and right icon in each panel represent the most and least typical member, respectively.

In summary, investigations of running quantitative assessments are continuing to: (i) determine a best initial parameter set for inclusion studies; and (ii) determine any improved efficiency in taxonomy selection from using visualization and editing tools. A refinement of the statistical-based package will become part of the commercial ASCAT product.

Summary of Results

To investigate the potential of the ASCAT to provide insight on the understanding the complicating effects of inclusions in the steel making process, and steel cleanliness of steel, a series of trials was performed with the Industry Partners. This section summarizes the findings from studies conducted during the course of this project.

MACSTEEL

MACSTEEL produces special bar quality (SBQ) steels using an electric arc furnace (EAF), ladle furnace, vacuum degassing and a billet caster. SBQ steels are a value added product used primarily in the automotive and other transportation industries. These steels are usually deoxidized with aluminum; often calcium treated and have a high level of control of alloying elements. With the recent acquisition of North Star Steel's Monroe Plant, MACSTEEL became the largest producer of SBQ steels in the USA.

There was an initial meeting with representatives of MACSTEEL in October 2000 to define a program to evaluate their products. A number of ladle and tundish samples were initially analyzed to demonstrate the capabilities of ASCAT, which illustrated that this technology would be useful. Based on the initial success, several projects were performed to examine a number of metallurgical problems. Listed below are examples of the work performed at the at MACSTEEL Jackson, MI facility.

Steel Cleanliness

In 2001, RJLG conducted a study to evaluate the overall cleanliness of their steels. The cleanliness was traced through the process and the ASCAT results were compared to the metallographic JK ratings. Approximately 80 samples were examined. The overall cleanliness of the SBQ steels produced at MACSTEEL was good as compared to other producers. The decrease in inclusions found in the steel through the various operating stages was documented. The results indicated they have no significant problems with reoxidation of the steel during processing.

Castability

In 2002, the ASCAT was used to examine the castability of Al-killed calcium treated steel. This is of importance to MACSTEEL because it is significantly more difficult to cast SBQ steel than flat rolled steel. First, the sulfur level is much higher (0.025-0.035%) for many SBQ steels for machineability. Secondly, the submerged entry nozzle (SEN) for a billet caster is much smaller than that for a slab caster. Over 120 samples from a large number of heats were examined using the special data acquisition and analysis techniques developed by RJLG for ASCAT. The analysis showed that the calcium treatment only converted the aluminum inclusions (Al_2O_3) to solid calcium aluminates (Al_2O_3 - CaO) and partial liquid inclusions, not the completely liquid inclusions required for castability. When calcium is added to these steels, it converts Al_2O_3 inclusions to Al_2O_3 - CaO and then the calcium reacted with sulfur forming CaS. Based on the findings a new calcium treatment process was developed to reduce the clogging.

Spinel Formation

For aluminum-killed steels, it is possible to form magnesium spinels which are magnesium and aluminum oxide (MgAl_2O_4) compounds. These spinels are very stable solid inclusions which can cause clogging. For good clean steel practices, the amount of reducible oxides (FeO and MnO) in the ladle slag are reduced to low levels. MACSTEEL has an excellent ladle slag with FeO plus

MnO less than 1.0%. This is called a "white slag practice" due to the color of the slag. Under these conditions spinels can form and spinels cannot react with calcium. ASCAT was used to investigate spinel formation. It was found that for some steels, the inclusions causing problems were spinels (MgAl_2O_4). Based on recommendations by RJLG, the slag practice was altered to keep the (FeO and MnO) content between 1% and 2%. The (FeO and MnO) in the slag reduces the amount of spinel formed.

NorthStar Steel

The North Star plant in Monroe, Michigan produces SBQ steel similar to MACSTEEL. Recently, the plant was purchased by MACSTEEL. RJLG used ASCAT to examine a number of metallurgical issues. One issue worth highlighting was a unique application of ASCAT; the examination of inclusions in SBQ steels deoxidized with Al and treated with titanium (Ti), calcium (Ca) and sulfur (S). The Ti is used to stabilize nitrogen as TiN and Ca is used to produce liquid calcium aluminates for castability and sulfur is added for the machineability of the bars. Thirty seven (37) samples from three heats were examined. The major inclusions were CaO - Al_2O_3 , spinels, some Al/Ti oxides and TiN. The results helped NSS to optimize their process to reduce the amount of inclusions.

LTV Steel

RJLG carried out an extensive study using the ASCAT to evaluate the inclusions found in high quality exposed automotive flat rolled steel. The inclusions were then related to the process and final products. The inclusions were complex and dependent on the process details. The inclusions included calcium aluminates (CA), duplex CA-CaS, spinels, and reoxidation products. The results were analyzed using the Ca - Al - S ternary diagrams and related to castability. The results were used to optimize the ladle and tundish practices to insure the inclusions were of the chemistry desired; specifically the practice produced liquid CA inclusions and reduced the amount of spinels and reoxidation inclusions. This was a major study and resulted in a publication² provided in the appendix. LTV was later acquired by ISG which in turn was acquired by Mittal Steel.

J & L Specialty Steel

One of the initial projects by RJLG using ASCAT was at J & L Specialty Steel. This project focused on the inclusions found in stainless steel. For this evaluation, samples were obtained from the AOD, trim station, tundish and coils. The ASCAT results were used to improve the gas bubbling or rinse procedures to reduce the amount of inclusions. Also, the cleanliness was examined for different tundish refractories and significant differences were found leading to improved cleanliness. The work at J & L indicated that ASCAT could be effectively used for stainless steel and lead to process and product improvements.

U. S. Steel Intensive Study

In addition to projects performed for MACSTEEL, LTV Steel, NorthStar and J&L Specialty Steel, an Intensive Study was conducted with U.S. Steel. The purpose of the Intensive Study was to investigate the potential of the ASCAT to provide insight on a wide variety of metallurgical issues. To date, over 2,500 samples have been analyzed using ASCAT technology.

Since the beginning of the ASCAT project, detailed inclusion analysis has been instrumental in solving numerous casting problems and helped provide direction on practices that improve quality at all five U.S. Steel domestic facilities. At this stage of development, it has been found that ASCAT is most useful as a diagnostic tool, where appropriate steel samples from the ladle, tundish and mold are analyzed and the results, summarized using various rules developed during the course of

the project, is compared to key process variables that are associated with the problem at hand. It is believed the accumulation of knowledge from these studies can then be applied to future generations of the ASCAT that are installed in the plant and provide close to real time feedback on inclusions, that can then be used to disposition cast product or detect ladle and casting processing issues which need to be corrected.

In total, through the life of the project, a total of thirty-two problems have been studied at all six domestic U.S. Steel steelmaking shops. The following summarizes twenty-seven of these studies and major findings from each:

Plant A

Castability Issues in Calcium Treated Grades

In 1999-2001, pouring of ladles of calcium treated grades at Plant A was stopped on a number of occasions due to clogging of the ladle gate. This caused return of steel in the ladle and in the worst-case unplanned terminations of casting lines. Through detailed inclusion analysis the causes of clogging and erosion were identified and practices corrected accordingly. The data obtained from these analyses was also used in a simplified form to help train operators. Since this time a significant reduction in this problem has been achieved.

On the opposite side to clogging, the consequences in terms ladle gate erosion due to excessive use of CaSi wire were demonstrated. The occurrence of excessive erosion and non-clean shut-offs of ladle gates is a significant safety and equipment damage concern. By designing practices to avoid excessive use of CaSi wire, savings were obtained in terms of reduced CaSi wire use. In addition, increased ladle pouring system refractory life was achieved.

Further details on this project can be found in the 2003 ISS steelmaking conference paper.¹

IF Degasser Grade Slag Conditioning Practice

At Plant A, a slag conditioning practice is carried out on degasser grades to control FeO levels in the ladle slag. Trials were conducted in which the slag conditioning practice was modified to reduce costs and emissions associated with use of Al-based slag conditioners. Based on detailed inclusion analysis coupled with coil surface quality inspection results, the revised slag conditioning practice was confirmed to maintain quality at levels similar or better than the previous practice. There were also benefits evident in terms of clogging due to reduction of the content of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel inclusions. Significant cost savings have been achieved from this project.

Clogging and Quality Issues in Rephosphorized Grades

Through detailed inclusion analysis on rephosphorized bakehard and Ti-stabilized ultra-low carbon grades, late FeP additions were identified as a significant source of Al_2O_3 inclusions and a prime cause of increased sliver rejections in exposed rephosphorized automotive bakehard grades (see 2004 AIST paper³). Based on this understanding, practices at Plant A have been changed to reduce or eliminate late FeP additions.

Behavior of Inclusions during Low Tundish Practices

On all four cast-lines at Plant A, slabs are downgraded when the tundish weight falls below set weight limits. Often these slabs are scrapped because few orders exist for lowest quality slabs. While low tundish weight slabs have higher Al_2O_3 inclusion content, this does not necessarily mean they are unsuitable for non-critical applications. After a low tundish event, knowledge of which slabs are produced with high inclusion content is very useful for dispositioning purposes. Inclusion analysis has demonstrated that factors such as tundish residence time also come into play, so tundish weight alone is not always the sole judge of the suitability of slab quality. Initial studies indicate that the low tundish weight downgrade can be altered to downgrade the slabs initially to an intermediate quality code and then to the lowest quality code at another lower weight.

TRIP (Transformation Induced Plasticity) High Al Steels

Over the last year two heats of a special new generation automotive high strength grade with high-Al TRIP Steel have been cast at Plant A. From these heats, mold and product samples were obtained. The goal was to understand inclusion formation in these steels along with processing strategies that avoid clogging.

D&I Tin Grade Heel Trials

Present practice on these grades calls for a ladle heel practice that results in the return of steel. This returned steel represents a yield loss, which represents a significant portion of overall yield losses. Initial inclusion analysis trials indicated that the heel could be reduced by 25-50% depending on the production facility using a special ladle bottom design. This project will continue to be a focus of future studies.

Tundish Flux Trials

Inclusion analysis was used to assess the impact of an improved tundish flux practice design to increase the $\text{CaO}:\text{SiO}_2$ ratio of the tundish slag. Analysis of Ti-stabilized ultra-low carbon grade inclusion content showed lower content of Al_2O_3 and $\text{Al}_2\text{O}_3\cdot\text{TiO}_2$ type inclusions when the revised practice was implemented. This verified the benefits of the practice and it was implemented as a standard.

Clogging in Motorlamination Grades

Through the first nine months of 2005, a significant amount of ultra-low carbon motorlamination grade steel was returned due to clogging of the ladle gate. This grade is highly alloyed and difficult to recycle in the shop. In addition, in the same time period, there were several unplanned terminations. All these factors were extremely disruptive to the shop and very costly. Based on the severe difficulties in pouring these grades, detailed inclusion analysis was carried in an effort to understand and solve this problem.

Based on the ASCAT inclusion analysis on mold samples from these grades, two factors were identified with respect to ladle materials and alloy quality. Neither of these findings was evident from any other measured chemistry or process variable. Two process changes were made based on these findings for production beginning in October 2005. Since these changes, there have been no incidences of returned steel due to clogging of the ladle gate.

Effect of Inclusions on Motorlamination Grade Magnetic Properties

A high content of small (2-5 micron) inclusions in electrical steels is known to be detrimental to magnetic properties, especially in 'higher end' applications. Work is ongoing to evaluate inclusion content in these grades and observe their impact on magnetic properties.

Plant B

Analysis of Clogging Behavior in Ti-containing Ultra-low Carbon Steels

Inclusion analysis helped identify the detrimental effect of late chill scrap, FeP and lime additions at the degasser in ultra-low carbon Ti stabilized grades. Practical elimination of chill scrap, FeP and lime as late additions halved the number of slabs downgraded due to clogging. Significant improvements in refractory life due to reduced clogging buildup were also realized from the changes brought about the understanding developed from inclusion analysis. Maximum tundish sequence was increased on all degasser grades and pouring tube life increased after these late additions were virtually eliminated. Further details are contained in the 2004 AIST paper³.

Clogging in Si containing non-CaSi grades

In early part of 2005, Plant B experienced significant problems with clogging in Si containing ERW (electric resistance welded) linepipe grades. In the worst case, clogging was severe enough to terminate one of the strands on the caster. Based on detailed inclusion analysis it was determined that alloy quality was responsible for clogging in these grades. By changing the alloy addition timing, the incidence of severe clogging in these grades was eliminated.

Final Argon Plug Ladle Rinsing Effects on Inclusions (Ti-stabilized Ultra-Low Carbon Grades)

Detailed inclusion analysis has helped define the benefits of final argon plug rinsing in Ti-stabilized ultra-low carbon grades produced at the RH-Degasser. These are the most critical grades produced by Plant B and most problematic from a clogging standpoint. Inclusion analysis showed final argon plug rinsing was most effective in removing larger Al_2O_3 inclusions.

ERW Hydrogen Induced Cracking (HIC) resistant steel practice development

Detailed inclusion analysis played an integral part in optimizing practices for the production of these critical linepipe grades. This work has allowed the possibility in the future to supply a new market of high end products, not presently made by U.S. Steel.

Plant C

Degasser Final Circulation

At the Plant C RH Degasser, it is customary to continue circulation after all alloys are added to facilitate further inclusion flotation. This stage of processing is called a 'circulation rinse'. Practices on ultra-low carbon IF grades called for five or seven minute circulation rinse depending on grade. Samples were collected at one-minute intervals during this circulation rinse and evaluated for inclusion content. Inclusion analysis showed little effect of circulation time beyond 3 minutes and above in duration. Based on this finding, the final circulation rinse has been cut to 3 minutes on most IF grades, saving 2 to 4 minutes per heat depending on grade. This time saving can translate into 2-3 extra heats per day through the facility. Further details on this study are contained in the 2004 AIST paper³.

Effect of Ar Purge on Inclusion Content during Initial Tundish Fill

Rapid sampling during tundish fill-up was conducted for Ar purge (normal practice) and non-Ar purge to measure any benefits from argon purging the tundish at startup.

Tundish Furniture Comparison

Inclusion analysis was used to assess the effects of a modified furniture arrangement incorporating a turbulence suppressor device. Results of inclusion analysis identified a problem with the modified arrangement and accordingly a further modification was made to address the issues identified. When this phase-two modified configuration was tested, inclusion analysis confirmed the modified arrangement maintained quality levels similar to the existing tundish design. Cost savings were achieved due to the modified design being cheaper to build than the existing design. None of these findings were evident from water models used to design the revised furniture configuration.

Tundish Flux Trials

Tundish flux trials incorporating the addition of SiO_2 based insulating fluxes (both rice-hulls and diatomaceous earth) to the existing basic tundish flux have been conducted. The main concern with these trials was to improve fluidity of the tundish flux while improving or maintaining the inclusion content. Trials indicated the altered practice is a slight improvement in terms of Al_2O_3 based inclusion content and issues with excessive crusting of the slag can be avoided.

Clogging in Degasser Si-containing Grades

Plant C experienced problems with clogging and unplanned terminations in two Si-containing grades produced through the RH-Degasser. Inclusion analysis identified alloy quality and high sulfur levels as causes for clogging in these grades. Accordingly, practices were altered to use alloys with a different purity along with the lower sulfur aim in the ladle. Since this time these grades have been produced with no casting problems reported.

Plant D

Tundish Furniture Trials

A revised tundish furniture arrangement incorporating a turbulence suppression impact pad was evaluated at Plant D during December 2004. Inclusion analysis results were similar to Plant C findings, with the revised configuration appearing inferior in terms of cleanliness compared to the standard arrangement. Based on these findings, it was decided to continue with the standard tundish furniture arrangement.

Al-based Slag Conditioning Trials

A series of heats were produced with and without slag conditioner added at the furnace. Samples have been analyzed from the tap ladle through to the mold and generally showed a progressive decrease in Al_2O_3 inclusion content. Slag conditioned heats were found to have a higher $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel content which is known to promote clogging. Work is continuing to evaluate this data with the aim of determining the benefit or otherwise of present slag conditioning practices.

Assessment of CaSi Practices

Based on earlier understanding of inclusion analysis Ca treated grades, detailed inclusion analysis was carried out on Plant D CaSi treated grades. This analysis was used to improve practices to avoid quality problems that had been experienced in these grades produced at Plant D.

Automotive Grade Low S Plugging

A critical low sulfur automotive grade experienced significant problems with ladle clogging. Due to low sulfur requirements, this grade was routed through the LMF and the desulfurization practices consequently resulted in a high content of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ inclusions that promoted clogging. As a result, the customer was contacted and permission was given to calcium treat these grades when produced through the LMF.

Plant E

Control of Tundish Slide Gate Erosion Behavior in Rounds Caster Grades

At Plant E erosion of the slide gate causes downgrades of Rounds destined for seamless pipe applications. Inclusion analysis showed the erosion was caused by Ca-rich inclusions (both oxide and sulfide based). Practices were changed to reduced this problem along with ZrO_2 inserted tundish slide gates which are more resistant to corrosion from CaO/CaS rich inclusions. This problem is further highlighted in the 2003 ISS paper¹.

Tundish Change Joint Cutoff

Detailed inclusion analysis was used to determine the possibility of reducing the crop-loss associated with tundish box change joints on slabs. It was confirmed that this was possible to reduce the crop size by approximately 50%, and accordingly practices have been changed.

Optimization of Environmental Cracking Resistance of Premium Seamless Pipe

Plant E produces a large quantity of pipe destined for critical applications for transport of oil and gas. These pipe are subject to a number of NACE type tests, including hydrogen induced cracking (HIC), and the DCB (double cantilever bending) tests. Preliminary work showed the results of these tests has a strong relationship to inclusion chemistry and content.

Study of Practices to Mid-Wall Inclusion Defects in Seamless Pipe

Seamless pipe destined to critical applications are usually ultra-sonically tested to detect the presence of any mid-wall inclusions. Inclusions that cause a rejection are large in size, however these large inclusions are often related to washouts of clogging buildups in the casting pouring system. The material that makes up these buildups originates from smaller inclusions in the melt. Detailed inclusion analysis is presently in use to determine inclusion baseline levels so that a series of steelmaking and casting process improvements aimed at reducing inclusion content and consequently the incidence of mid-wall inclusions can be assessed.

Optimization of Degasser Usage on Pipe Grades

For certain premium pipe grades, the ladle-lid degasser is used at Plant E as part of a standard practice designed to produce clean steel. The actual benefit in terms of steel cleanliness of mandatory degas processing has not been previously quantified. Given that operation of the degasser represents an additional cost (vacuum system operating cost and temperature loss),

detailed inclusion analysis using ASCAT will be used to measure any impact of degassing on inclusion content.

Accomplishments

The objective of this study was to develop the technology to permit steelmakers to provide insight on the complicating effects of inclusions to allow the steel producers to increase product throughput, better control the process, reduce remelts, and improve the quality of the product. To meet this objective, the ASCAT was developed. Working with steel industry leaders, the ASCAT was demonstrated to be more than capable of meeting the original objective; a number of the world's largest steel companies discovered that the ASCAT enabled better overall management of the steel making process, resulted in production of higher quality steel, and increased production throughput. Representatives of the steel industry have stated that the ASCAT is a "totally unique" system.

Several papers were published describing use of the ASCAT in numerous applications of interest to steel industry. One of the papers was awarded the AISI Medal in 2004. This award is only given to one technical paper each year having special merit and importance in connection with the activities and interest of the iron and steel industry.

An independent evaluation performed during the course of the project concluded that the ASCAT will be *clearly superior in performance and features* than anything being presently tried by U.S. steel producers.

With respect to intellectual property (IP), RJLG is working with its patent attorney to obtain patents on certain features of the ASCAT that involve electron beam positioning decisions based on minimum analytical information. The result is a new paradigm of speed and efficiency of analysis, enabled by innovative low-level interfacing between the analysis system and the electron microscope. We are in the process of filing two provisional patent applications. Patent searches have been completed on (1) EDSEM - Efficient acquisition of multi-resolution X-ray maps with extensions to acquisition of sparse, feature-oriented spectral images; and (2) unique Spectral Image acquisition method. The patents are sought to protect against X-ray analysis companies taking advantage of our innovations.

Two additional patents were conceived as a result of implementing and attempting to improve the data acquisition technology underlying the ASCAT instrument. An initial patentability search by our patent attorneys indicates that both concepts are patentable:

1. "Detecting Density Transitions during High-Speed Electron Beam Scanning"
2. "Dynamically Classifying Objects by X-Ray Emission Spectroscopy"

In addition to patents, RJLG has entered into an agreement with TESCAN to produce the SEM hardware for the ASCAT (the current version is based on a Tescan SEM). TESCAN is a private company based in the Czech Republic that specializes in the design and manufacture of scanning electron microscopes. TESCAN combines the experience of leading scientists and research technicians with the innovative and creative attitude of young, highly-educated people to keep it position among the leading companies in the field of electron microscopy.

Conclusions

The ASCAT represents an innovative new tool for the collection of statistically meaningful data on inclusions in a steel sample, and addresses a market need to monitor the effects of inclusions in the steel making process. ASCAT technology permits acquisition of inclusion size and composition data at a rate never before possible in SEM-based instruments, and represents a quantum leap in inclusion analysis that will allow steel producers to evaluate the quality of steel and implement appropriate process improvements. In terms of performance, the ASCAT: (1) allows for accurate classification of inclusions by chemistry and morphological parameters, (2) can characterize hundreds of inclusions within minutes, (3) is easy to use (does not require experts), (4) is robust, and (5) has excellent image quality for conventional SEM investigations (i.e., can be used as a dual use instrument).

In studies conducted with steel producers, the use of ASCAT has resulted in increased production and reduced downgrades, resulting in significant savings (>\$1M/year/installation) to the bottom line. Thus, the value proposition to steel producers is that they can reduce the cost of production, as well as increase the production of high-grade steels and alloys significantly. Because the ASCAT directly impacts both bottom line and product quality, payback can be calculated in months given the correct understanding of the data. To this end, the commercial ASCAT package includes not only the tool, but the necessary consulting and training to help the customer utilize the technology effectively.

With respect to energy savings, the ASCAT greatest contribution will be related to reducing the need to perform remelts. Re-melt energy consumption is estimated at 460 kWh/ton or 1.6 million btu. Assuming 110 million ton capacity and 90% utilization with approximately 40% in the targeted high-grade and specialty steels, yields ~40 million tons of total market. Direct energy savings of ASCAT at 100% market penetration with 0.5% remelt industry-wide would be 200,000 tons x 1.6 million btu/ton = 3.2×10^{11} btu or 0.25% of steel industry energy consumption.⁸

With respect to commercialization, it has been demonstrated that the ASCAT will significantly advance the tools of the industry and addresses an urgent and broadly recognized need of the steel industry. In the current configuration of the ASCAT as a laboratory tool used to evaluate process and quality, we can estimate that there are on the order of 50 locations world-wide that would have the justification and resources to buy an ASCAT tool. If the ASCAT can be developed into a near real-time tool and its benefits established, the number of potential units will increase to several hundred. To this end, we are planning on commercializing both a laboratory version and a production version of the ASCAT (see Figure 7).

⁸ Chan, I., Engle, D.C., and N. Margolis, Collaborative R&D Partnerships Between the U.S. Dept. of Energy's Office of Industrial Technologies and the Steel Industry, *AISE Steel Technology*, October 2003.

Figure 7. Process Flow Diagram Illustrating the Application of the ASCAT as a Production Tool and Laboratory Instrument.

Recommendations

Results of this study clearly indicated that the ASCAT will significantly advance the state-of-the-art in inclusion analysis in metal samples and addresses a broadly recognized need of the steel industry. Based on the success of this program, it is recommended that marketing and sales activities be initiated focusing initially on the laboratory version of the ASCAT, and that efforts continue on the development of a production version of the ASCAT. It is also recommended that ARTClass be integrated as part of the standard ASCAT product package. Further, it is recommended that methods be developed to automatically apply problem-specific information to help select the optimum inclusion class partitions, to minimize direct intervention from experts.

The market that we will initially focus sales of the laboratory version of the ASCAT is a subset of the metal cleanliness market (see Figure 8). The initial segment of interest is the Primary Metals Producers/Steel. Within the primary metals producers/steel segment, we currently have three active prospects for orders to be placed in 2006. Studies are also currently being conducted with an aluminum company.

Figure 8. Diagram illustrating potential Metals Cleanliness markets for the ASCAT

References / Bibliography

G.A.Carpenter and S.Grossberg (1987), "ART2A: Stable self-organization of pattern recognition codes for analog input patterns. *Applied Optics* 26 4919-4930.

L.Kaufman and P.J.Rousseeuw (1990) Finding Groups in Data: An Introduction to Cluster Analysis, New York: John Wiley.

G.A.Carpenter, S.Grossberg, and D.B.Rosen, (1991) "ART-2A – An adaptive resonance algorithm for rapid category learning and recognition." *Neural Networks*, 4 493-504.

J.I.Goldstein, D.E.Newbury, P.Echlin, D.C.Joy (1992) Scanning Electron Microscopy and X-Ray Microanalysis: A Text for Biologists, Materials Scientists, and Geologists (2nd Ed.) Kluwer Academic / Plenum Publishers. p382ff.

Y.Xie, D.Wienke, and P.K.Hopke (1994) "Airborne particle classification with a combination of chemical composition and shape index utilizing adaptive resonance neural networks." *Environ. Sci. Technol.* 1921-1928.

D.Wienke and G.Kateman, (1994) "Adaptive resonance theory based artificial neural networks for treatment of open-category problems in chemical pattern recognition – application to UV-, Visible- and IR spectroscopy, *Chemometrics and Intelligent Laboratory Systems*, 23 309-329.

D. Wienke, Y. Xie, and P.K. Hopke (1995) "An adaptive resonance theory based artificial neural network (ART-2A) for rapid identification of airborne particle shapes from their scanning electron microscopy images." *Chemometrics and Intelligent Laboratory Systems* 25 367-387.

R.D.Reed and R.J.Marks,II (1999) Neural Smithing: Supervised Learning in Feedforward Artificial Neural Networks. The MIT Press, Cambridge, Mass.

X-H Song, L.Hadjiisji, P.K.Hopke, L.L.Ashbaugh, G.S.Casuccio, and S.Schlaegle (1999) "Source apportionment of soil samples by the combination of two neural networks based on Computer Controlled Scanning Electron Microscopy." *J. Air Waste Manag. Assoc* 49 773-783.

Appendices

- Story, S.R., Piccone, T.J., Fruehan, R.J., and Potter, M., "Inclusion Analysis to Predict Casting Behavior," *Iron & Steel Technology*, Sept. 2004, pp. 163-169.
- Story, S.R., Smith S.M., Fruehan, R.J., Casuccio, G.S Potter, M.S., and Lersch, T.L., "Application of Rapid Inclusion Identification and Analysis," *Iron & Steel Technology*, Sept. 2005, pp. 41-49.
- Ahlborg, K., Fruehan, R.J., Potter, M., Badger, S., and Casuccio, G., "Inclusions in Aluminum-Killed Steel with varying Calcium Additions," *ISSTech 2003 Conference Proceedings*, Vol. 2, pp. 177-194.

Inclusion Analysis to Predict Casting Behavior

THIS ARTICLE IS AVAILABLE ONLINE AT WWW.AIST.ORG

There is an increasing demand for cleaner steels with low inclusion content, and the inclusions in the steel often must have defined properties. The composition, and hence the properties, of the inclusions can be controlled through the chemistries of the metal and slag. Despite the major advances in our knowledge of inclusion control, there is currently no rapid and accurate method for determining the type, size and number of inclusions present. Usually, a postmortem analysis is performed on samples using a scanning electron microscope (SEM) or conventional metallography long after the steel has been processed. Also, in any given sample, there are inclusions of varying chemistry present, and an analysis of a single or even several inclusions may not truly reflect the cleanliness or the type of inclusions present. To overcome these problems, the R.J. Lee Group and a number of partners, including several steel companies, with a grant from the U.S. Department of Energy, are developing an Automated Steel Cleanliness Analysis Tool (ASCAT). It is designed around a computer-controlled scanning electron microscope (CCSEM) and is capable of analyzing several hundred inclusions rapidly.

The goal of the ASCAT is to prepare a sample, perform a complete analysis of the inclusions with respect to size and chemistry, and report the results to the operator in a clear, simple manner in less than one hour. One of the tasks of the overall project is to analyze the data rapidly and to display the results in such a manner that will clearly indicate to the metallurgist or operator whether the steel and/or process are satisfactory. If the heat is not satisfactory, it could be corrected or the heat could be downgraded before costly downstream processing, and the problem could be prevented in subsequent heats. In this article, steel samples obtained from U. S. Steel Gary Works and Fairfield Works were examined using the CCSEM, and the inclusion charac-

teristics were related to the casting performance of the steel.

Fundamental Metallurgy

As discussed elsewhere in detail,¹⁻³ when calcium is added to steel, it can modify alumina (Al_2O_3) inclusions to calcium aluminates or react with sulfur to form CaS. The calcium aluminates can be solid or liquid at steelmaking

Techniques are being developed to rapidly identify inclusions in steel so that potential problems can be addressed. Here, casting-related issues at U. S. Steel Gary and Fairfield Works are examined in order to discover the causes of clogging and to predict casting behavior and erosion.

temperatures. For example, $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ (CA_6) has a melting point of $1,833^\circ\text{C}$,⁴ whereas the eutectic temperature between $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ (C_3A) and $\text{CaO} \cdot \text{Al}_2\text{O}_3$ (CA) is only $1,362^\circ\text{C}$.⁴ In general, liquid inclusions are desired to avoid clogging during casting and the occurrence of large alumina clusters in the product. The governing chemical reaction determining what inclusions form can be written as:

The parentheses indicate that the species is part of an inclusion. If the Al and/or S content is high, the reaction shifts to the left, and solid inclusions and calcium sulfide form. However, if Ca usage is extensive, there will be excessive Ca-rich inclusions, which can cause nozzle or ladle gate erosion.

Fourteen calcium-treated Al-killed heats made at Gary Works representing ladle gate

Authors

Scott R. Story (left), senior project research engineer, and Thomas J. Piccone (center), senior research engineer, U. S. Steel Corp. Research and Technology Center, Monroeville, Pa.; Richard J. Fruehan (right), U. S. Steel Professor, Materials, Science and Engineering Dept., Carnegie Mellon University, Pittsburgh, Pa.; and M. Potter, R.J. Lee Group, Monroeville, Pa. (srstory@uss.com)

Figure 1

Liquid oxide inclusion region indicated on a $\text{CaO-Al}_2\text{O}_3\text{-S}$ ternary phase diagram.

behavior associated with clogging, erosion and stable casting (i.e., neither clogging or erosion) were analyzed to determine whether the casting performance could be related to the inclusions present. To examine the inclusions in these types of steels, a technique was developed in which the inclusion composition is plotted on a Ca-Al-S ternary diagram. In general, the inclusions are duplex, consisting of a calcium aluminate phase and a calcium sulfide phase. Once an inclusion is identified as an oxide inclusion containing these elements, the composition is normalized to these elements. The boundaries for liquid oxide inclusions are shown in Figure 1. The left boundary is shown at a value of 0.4 mole fraction Al, but may be closer to 0.45, according to a published phase diagram.⁴ If the inclusion composition is to the right of the right boundary, plugging or clogging may occur; in the liquid region, casting should be stable; and, to the left, erosion may occur.

Another method of determining whether stable casting conditions may be expected is to examine the Ca/Al ratio. The Ca/Al ratio should take into account the amount of Ca combined with S in the inclusions. Therefore, a "modified Ca/Al ratio" was developed. At high values of Ca/Al ratio, erosion may occur, while clogging may occur at low values. Initially in this study, a simple arithmetic average of the Ca/Al ratio was used. However, often the smaller inclusions tend to contain more Al. Another value of the modified Ca/Al ratio based on area was later developed.

A second series of Ca-treated Al-killed heats from Fairfield Works was examined. In this case, the steel was solidified in a rounds caster, and the samples were from the solidified steel. The concern here was erosion of the tundish slidegate. It is believed that, if the gate is highly eroded, there may be air ingress, causing reoxidation of the steel or the formation of

large nonequilibrium inclusions. The physical size of the samples for the SEM is small, and the probability of having one of these large reoxidation products is small, i.e., it is akin to looking for a needle in a haystack. Nevertheless, it may be possible to know whether erosion is occurring by examining the normal small inclusions.

Due to reactions that occur during solidification, inclusions in cast product steel samples are expected to show compositional differences compared to those analyzed from quenched liquid steel samples. It has been shown that during slow solidification, the inclusions will be pushed ahead of the solidification front. Due to enrichment of Al and S in the liquid portion during solidification, the equilibrium for Equation 1 shifts to the left, increasing the Al content of the inclusions.⁵ Therefore, any analysis of the casting behavior based on the ternary diagrams or the Ca/Al ratio should be for quenched liquid steel samples. For caster solidification, an empirical correction to the Ca/Al ratio may be possible that will characterize the inclusions that were present in the liquid steel.

In the Gary Works heats, the samples were from the liquid steel, while those from Fairfield Works were from the solidified steel. Therefore, the ternary diagrams and the uncorrected Ca/Al ratio possibly cannot be used for the Fairfield Works samples. In the preliminary analysis of the results, it was found that the amount of erosion was proportional to the area of CaS inclusions. Based on these findings, a CaS window in the Ca-Al-S diagram, as indicated in Figure 1, was developed to define inclusions with large amounts of CaS.

It is believed that the reason CaS or Ca-rich inclusions cause erosion is that Equation 1 occurs on the alumina nozzle, thereby dissolving alumina. It is often found that CaS is in the material, clogging a nozzle. The authors believe that this occurs when the sulfur content is high (> 0.01 percent) and a mixture of solid $\text{CaO} \cdot \text{Al}_2\text{O}_3$ (CA) and CaS clog the nozzle. In the present case, the sulfur is low, typically less than 0.003 percent. In this case, due to high levels of Ca combined with low sulfur, CaS along with Ca-rich calcium aluminate inclusions form, both of which have the potential to dissolve alumina-based refractories.

Steel Processing

The samples examined from Gary Works were from a range of calcium-treated heats that displayed signs of either plugging, stable casting or erosion behavior of the ladle slidegate. The samples used in this section of the study were taken from the mold, generally at ladle shutoff, which is the point at which approximately 80 percent of the heat has

been cast. The majority of calcium-treated heats at Gary Works are unskimmed, and calcium carbide and lime-rich flux additions are used to adjust slag composition to achieve lime saturation and low FeO + MnO levels. For ultralow sulfur heats (≤ 0.003 wt.% S), or if the heat is not sufficiently killed on tap, the heat is skimmed and a new slag is built from lime and calcium aluminate additions. At the LMF, CaSi wire is injected as the final addition during processing, with a subsequent three-minute argon rinse before the heat is shipped to one of the three slab casting machines. In the heats that exhibited clogging tendency, restriction of steel flow was most evident in the behavior of the ladle slidegate. Clogging of the ladle slidegate has productivity and quality implications due to steel being returned in the ladle and subsequent disruption of process flow in the shop. Therefore, the clogging/erosion behavior was studied by examining the variation of the ladle slidegate position normalized against caster mold throughput.

At Fairfield Works, all heats produced on the 4-strand rounds caster are CaSi-treated to assure castability of the heat due to the small section pouring refractories used to feed each of the four caster molds. The samples used in this study were selected from ultralow sulfur heats (≤ 0.003 wt.% S), where additional CaSi wire additions are made early in the processing at the LMF to assist in desulfurization. After processing is complete at the LMF, these heats are normally routed to a ladle-lid degasser, and then on to the caster. Since this study was conducted on heats some time after they had been originally cast, samples used in this section of the study were taken from the cast product samples that were available. Tundish slidegate erosion rates of each round are tracked in real time. When erosion is excessive, depending on product application, individual rounds may be downgraded to lower-quality applications. The erosion index used in the Fairfield Works study was calculated by determining the movement in gate position (in millimeters) away from a theoretical uneroded position for each 100 feet cast.

Computer-controlled SEM Analysis

Briefly, the CCSEM analyses were performed using an ASPEX Instruments personal SEM-75 microscope equipped with a Gresham light element energy-dispersive spectrometer (EDS). In addition, all analyses were performed with an accelerating voltage of 20 KeV in backscattered electron imaging mode. Computer-controlled scanning electron microscopy provides simultaneous measurement of individual inclusion size, shape (aspect ratio) and elemental composition by combining an SEM, an x-ray analyzer (EDS)

and a digital scan generator under computer control.

Inclusions were detected on the polished steel sample by moving the electron beam in discrete increments ("x, y" pattern) across the sample and monitoring the resultant backscattered signal to determine when the electron beam was on an inclusion. A low grid point density was used in the search mode, thereby increasing the area of the sample to be analyzed per unit time. Once a coordinate was reached where the signal was above the threshold level, the computer switched to the "acquire" mode, and the electron beam was driven across the inclusion in a preset pattern using a higher (more closely spaced) grid point density to determine the size of the inclusion. The average, maximum

Figure 2

Inclusion composition of a heat that had stable casting.

Figure 3

Inclusion composition of a heat that had ladle gate erosion.

Figure 4

Inclusion composition of a heat showing ladle gate clogging.

Figure 5

Inclusion composition of a heat that had slight ladle gate erosion.

and minimum diameters were recorded during the analysis.

The analysis continued until each inclusion achieved a 0.45-second x-ray acquisition time (~1,200 x-ray counts). At the completion of the x-ray analysis, the computer interpreted the resultant spectrum to determine which elements were present. The elements present in the spectrum were then processed to obtain their relative concentrations. Elements monitored during the CCSEM analysis included oxygen (O), magnesium (Mg), aluminum (Al), silicon (Si), sulfur (S), chlorine (Cl), potassium (K), calcium (Ca), titanium (Ti), chromium (Cr) and manganese (Mn).

Between 325 and 1,500 inclusions were analyzed from each sample. This included scan-

ning a sample area of 133 mm² at a magnification of 100X and analyzing all inclusions greater than 2 µm in size.

Results and Discussion

Gary Works Samples — The results from the 14 Gary Works heats showed a definite pattern. The results of the inclusion composition on a Ca-Al-S ternary diagram are shown in Figures 2–4 for typical stable, eroding and clogging heats, respectively. When casting was stable, a significant portion of the inclusions fell within the liquid region, as shown in Figure 2. When there was erosion, the inclusion compositions were to the left of the liquid region (Figure 3), and compositions were to the right for clogging (Figure 4). These three heats showed clear evidence of stable casting, erosion or clogging, and the inclusion compositions clearly reflected this. Even in marginal cases, the inclusion compositions reflected the casting performance. For example, the inclusions for a heat with slight erosion are shown in Figure 5. The inclusions are only slightly to the left of the liquid region as compared to Figure 3, and therefore slight erosion is expected.

Considering that some of the Ca is present as CaS, the theoretical parameter that will indicate the type of oxide present is given by:

$$"Ca/Al" = \frac{Ca - (S - 2)}{Al} \quad (\text{Eq. 2})$$

where *Ca*, *Al* and *S* are the Ca, Al and S content of the inclusions respectively (atomic %).

This parameter has been defined as the "modified Ca/Al ratio" to account for CaS in the duplex inclusions. The deduction of sulfur accounts for Ca as CaS. The number 2 in Equation 2 represents the approximate solubility of S in liquid calcium aluminates. In theory, at 1,600°C, this ratio should be between approximately 0.5 and 1.5 for the oxide portion of the inclusions to be liquid. However, in the upper end of this range, erosion may occur. The present case may be affected by the shift to Al-rich inclusions during solidification, but the shift is small for quenched samples.

In Figure 6, the results are plotted versus the modified Ca/Al ratio. Both the numerical average and the area-weighted average of the Ca/Al ratio are shown. The area ratio was only slightly lower than the numerical average, but should be more representative. The results indicate that stable casting is achieved when the ratio is greater than 0.4, which is in the two-phase region, liquid plus solid CaO·Al₂O₃. Erosion occurred when the ratio exceeded about 0.8, which is toward the center of the liquid region for the CaO·Al₂O₃

Figure 6

system at steelmaking temperatures. As indicated in Figure 6, below a Ca/Al ratio of 0.4, plugging of the ladle slidegate occurred at varying points within a heat. Plugging was observed to occur toward the middle of a heat when the Ca/Al ratio was in the range of approximately 0.2–0.4. With Ca/Al ratios of less than 0.2, plugging of the ladle gate was evident almost immediately after the ladle was opened.

In one heat, a large fraction of the total inclusion area was from inclusions containing Na, which is indicative of mold slag. This is important in itself, indicating the entrainment of slag from improper pouring or sampling practices. Also, in this case, this fraction of the inclusions should not be included in computing the Ca/Al ratio, since it skews the results to a generally higher Ca/Al ratio. Based on this, whenever there is evidence of tundish or mold slag, it is reported on the summary sheet.

Review of heat log information showed that heats associated with ladle gate clogging had, in general, a larger than normal Al loss or fade from the ladle to the caster mold. For the stable heats, the percentage of Al lost during processing was typically 10–20 percent, and possibly less for those heats where there was erosion. When there was plugging, more than 30 percent and often more than 50 percent of the Al was lost from the steel. In addition, for heats showing a clogging tendency, the Ca content of the steel was also generally lower than normal. Both the low Ca and high Al loss indicate that reoxidation of the steel is the likely cause of the clogging. Unstable oxides, such as FeO, in the ladle slag or exposure of the steel to air due to excessive Ar bubbling will cause Al to be oxidized and increase the Al_2O_3 content of the calcium aluminate inclusions. Subsequent to these findings, practices have been modified to further reduce FeO levels in the ladle slag in calcium-treated heats. Knowledge of the consequences of reoxidation in Ca-treated heats has also directed attention toward avoidance of excessive stirring, especially after the addition of CaSi wire. In the time since these changes, the occurrence of plugging in CaSi heats has been practically eliminated.

Fairfield Works Samples — As mentioned previously, there was a relationship between the area of CaS inclusions and the erosion index, as shown in Figure 7. For these heats, the presence of excessive amounts of CaS or Ca in the inclusions indicates that erosion of

The modified Ca/Al ratio corrected for sulfur for Gary heats, indicating casting performance.

Figure 7

Erosion index as a function of the area of CaS inclusions for Fairfield Works heats.

an alumina nozzle will occur. It should be noted that this analysis should not be applied to steel with high sulfur contents (> 0.008 percent S). At high sulfur contents, CaS will form, but not liquid calcium aluminates. In this case, the Al and S levels are too high to allow Equation 1 to go to the left. Solid oxide inclusions such as Al_2O_3 or $\text{CaO} \cdot \text{Al}_2\text{O}_3$ will clog the nozzle along with CaS.

Previous studies at Fairfield Works⁶ have shown that tundish slidegate erosion is linked to reduced cleanliness levels in the cast product, possibly due to occurrence of

Figure 8

Inclusions from a typical Fairfield heat showing high erosion on a $\text{CaO-Al}_2\text{O}_3\text{-S}$ ternary phase diagram.

Figure 9

Inclusions from a Fairfield heat showing low erosion on a $\text{CaO-Al}_2\text{O}_3\text{-S}$ ternary phase diagram.

air aspiration, which causes reoxidation and consequent formation of large nonequilibrium inclusions such as silicates or alumina inclusions. No significant increase in these types of inclusions was found in the heats that had erosion. The number of these inclusions per unit area would be very small; therefore, it is highly unlikely that they would be found in a typical SEM sample, so the observations with regard to these inclusions are reasonable.

The samples from Fairfield Works were taken from the solidified product. As discussed, this will lead to an enrichment of Al_2O_3 in the inclusions. The inclusions plotted on the ternary diagram are shown in Figures 8 and 9 for typical heats that demonstrated high and low slidegate erosion, respectively. In all three cases, the inclusions are on the right side of the liquid region, and this is

indicative of clogging, not eroding, heats. The inclusion compositions of samples from the final product are not directly comparable to the criteria for casting performance developed from the Gary data due to Al_2O_3 enrichment of the inclusions during solidification. A sample taken from a heat of liquid steel that had this modified Ca/Al ratio would indicate clogging, not erosion. Other heats causing erosion showed a similar behavior with regard to inclusion composition. Obviously, the rules developed for samples of liquid steel that worked well for the Gary heats cannot be applied to steel solidified in the caster.

A critical question is, Why did some of the heats experience higher levels of erosion than others? The Al and S contents of all of the heats were similar. The amount of CaSi injected was similar in all cases, and no correlation between the amount of CaSi used and the slidegate behavior was found. A reasonable relationship was found between the area fraction of CaS inclusions and the time period between the initial CaSi addition and casting (defined as the time when steel corresponding to the sample solidified in the mold), as shown in Figure 10. The results indicate that reoxidation of the steel occurs after the CaSi addition — probably by reaction with unstable oxides such as FeO, MnO and SiO_2 — in the ladle slag. As reoxidation occurs, enrichment of Al_2O_3 in the inclusions increases with time, which reduces the potential to form Ca-rich sulfide and oxide phases during solidification.

Understanding of the cause of slidegate erosion in Fairfield ultralow sulfur heats has helped researchers to develop strategies to eliminate the problem. For instance, corrosion-resistant slidegate refractories (i.e., zirconia insert plates) have been installed for use during production of ultralow sulfur rounds heats.

Conclusions

This article demonstrates that the ASCAT is a valuable tool in identifying casting problems and their causes. The results from trials at Gary Works show that inclusion compositions from samples of the liquid steel plotted on a Ca-Al-S ternary phase diagram will predict if there will be stable, eroding or clogging conditions during casting. The modified Ca/Al ratio is also a good predictor of casting behavior. The results also helped to identify the likely source of clogging caused by solid Al_2O_3 -rich calcium aluminate inclusions, which may have been caused by excessive argon stirring or oxidizing ladle slag that caused reoxidation.

The samples from Fairfield Works were from the solidified steel, in which case the Ca-Al-S diagrams are not useful in identifying

casting conditions due to Al_2O_3 enrichment of the inclusions caused by the enrichment of Al and S during solidification. However, the area of CaS inclusions could be used to predict the amount of erosion of the tundish slidegate. This finding helped to identify the possible cause of the problem, which has assisted in developing solutions that eliminate the occurrence of erosion.

Techniques have been developed to provide both the operator and metallurgist with the critical information clearly on a single page. Examples are shown in Figures 2–5. The inclusion compositions and sizes are shown on a Ca-Al-S ternary diagram. This allows the metallurgist to quickly check sizes of the inclusions and assess whether proper modification by the calcium treatment has been achieved. Also on the sheet is the total area of oxide inclusions (which is a measure of cleanliness), the average value of the Ca/Al ratio, and whether Mg-spinel or mold/tundish slag inclusions are present.

The objective of the ASCAT is to help the steelmaker improve operations. Analyses of samples from the as-cast steel are obtained too late to save the heat. However, they may be useful in deciding how the slabs or blooms are processed and applied to specific orders. Also, the inclusions in samples from the as-cast steel have different inclusion compositions than those in the liquid steel before casting. The application of the ASCAT is best for samples taken from the liquid steel. For example, in the case of the Gary Works heats, samples from the ladle may indicate the need for corrective action, such as another CaSi addition. It could also indicate a processing problem, such as excessive reoxidation caused by unstable oxides in the ladle slag and/or excessive Ar rinsing.

Acknowledgments

The authors wish to acknowledge the U.S. Department of Energy Office of Industrial Technology (DOE Cooperative Agreement No. DE-FC07-99ID13820) for their support in this work. The authors would also like to thank Gary and Fairfield Works operating and quality assurance personnel who provided samples and data used in this study.

This paper was presented at ISSTech 2003 in Indianapolis, Ind.

Figure 10

Effect of residence time from initial CaSi injection to casting on CaS area fraction for heats with no late CaSi addition.

References

1. Fruehan, R.J., ed., "Calcium Treatment and Inclusion Modification," *The Making, Shaping, and Treating of Steel, Steelmaking and Refining Volume*, AISE Steel Foundation, Pittsburgh, Pa., 1998, pp. 150–151, 687–692.
2. Larsen, K., and Fruehan, R.J., "Calcium Modification of Oxide Inclusions," *Iron & Steelmaker*, Vol. 17, No. 7, July 1990, pp. 45–52.
3. Ahlborg, K.; Fruehan, R.J.; Potter, M.; Badger, S.; and Casuccio, G., "Inclusions in Aluminum-Killed Steel with Varying Calcium Additions," *ISSTech 2003 Conference Proceedings*, Vol. 2, pp. 177–194.
4. Eriksson, G., and Pelton, A.D., "Critical Evaluation and Optimization of the Thermodynamic Properties and Phase Diagrams of the $\text{CaO-Al}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-SiO}_2$ and $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ Systems," *Metallurgical Transactions B*, Vol. 24B, No. 5, Oct. 1993, pp. 807–816.
5. Wang, Y.; Valdez, M.; and Sridhar, S., "Formation of CaS on $\text{Al}_2\text{O}_3\text{-CaO}$ Inclusions During Solidification of Steels," *Metallurgical and Materials Transactions*, Vol. 33B, No. 4, Aug. 2002, pp. 625–632.
6. Perkins, C., and Flynn, K., "Bloom Cleanliness Correlated to LMF and Casting Parameters," *Steelmaking Conference Proceedings*, Vol. 78, Iron & Steel Society, 1995, pp. 431–438. ♦

Application of Rapid Inclusion Identification and Analysis

To identify potential problems associated with inclusions in the steelmaking process and final products, techniques are being developed to rapidly identify inclusions in steel. Understanding the origin of inclusions and developing practices to control their composition and content in liquid steel are key to improved castability and quality. The inclusion analysis technique used in this work was based on a computer-controlled scanning electron microscope known as the Automated Steel Cleanliness Assessment Tool (ASCAT). ASCAT can determine the size and composition of hundreds of inclusions in less than 30 minutes. The overall aim of this work is to develop a system that can provide the metallurgist with rapid feedback on inclusion characteristics so that problems can be quickly identified and corrected. In order to develop software and expert systems to analyze the results, a variety of steelmaking issues related to inclusions are being examined.

In this article, three examples of application of this inclusion analysis approach are discussed. In the first example, the very strong influences between late oxidizing alloy additions to Ti-stabilized ultralow-carbon (Ti-ULC) grades and caster clogging are demonstrated. In the second, the impact of degasser circulation time after final alloy addition in Ti-ULC grades on inclusion content is examined. This work was used to determine the rinse circulation time, depending on the product application, which provides the best compromise between cleanliness and productivity. Last, some recent understanding on the origin of $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel inclusions in low-carbon grades produced through the ladle metallurgy facility (LMF) is discussed. This type of inclusion is known to have a strong influence on clogging. Inclusion analysis has indicated that their formation is promoted by arcing at the LMF and slag with lower levels of reducible oxides, particularly FeO.

In today's global steel market, the need for improving steel cleanliness and engineered inclusions is ever increasing. Despite advancements made in the study of inclusion modification, or inclusion engineering, the ability to understand fully the micro-characteristics of the inclusions and relate them to the macro-characteristics of a given steel in a near-real-time fashion does not exist. Typical analyses of

ASCAT, an automated steel cleanliness analysis tool, can determine the size and composition of hundreds of inclusions in less than 30 minutes. ASCAT's application to a number of metallurgical concerns is presented.

steel using conventional metallography usually occur days, weeks or even months after a heat has been cast, and therefore the data cannot be used in the evaluation of production problems or quality issues in a timely fashion.

Many of the problems associated with steel production result from a multitude of complex inclusion types. Different compositional types are created for varying reasons, and their compositions can lead to different problems. This fact has led to the struggle that arises from analyzing a sample with optical microscopy. The visual assessment of a "large" area of the sample does not give a complete understanding of the chemical types of inclusions present. Scanning electron microscopy, on the other hand, can provide the needed compositional analysis, but historically has been limited to characterizing only a few inclusions covering a "small" area.

In the quest to find a solution to this problem, the RJ Lee Group is developing computer-controlled scanning electron microscopy (CCSEM) analysis techniques capable of analyzing hundreds of inclusions in a steel sample

Authors

Scott R. Story (left), senior project research engineer, and Samuel M. Smith, research manager, U. S. Steel Corp. Research and Technology Center, Monroeville, Pa. (srstory@uss.com); Richard J. Fruehan (center), U. S. Steel professor, Materials Science and Engineering Dept., Carnegie Mellon University, Pittsburgh, Pa.; Gary S. Casuccio, vice president, Michael S. Potter (right), materials scientist, and Traci L. Lersch, materials scientist, RJ Lee Group Inc., Monroeville, Pa.

Figure 1

Process of inclusion analysis and identification: (1) inclusion detected and sized; (2) spectrum is analyzed, i.e., percentages of each element determined; (3) spectrum data processed through CCSEM rules; and (4) based on percentages, a classification is assigned.

in a matter of minutes. The second component of this work is directly relating the inclusion data to key steelmaking, casting or quality parameters. This effort is funded in part by the U.S. Department of Energy, through the "Development of the Automated Steel Cleanliness Analysis Tool (ASCAT)" project. The goal of this project is to develop a system that can take a steel sample obtained from a given point in the steelmaking process, prepare it to a "just good enough" finish, analyze it in an SEM and report the results in near-real-time fashion.

As part of this work, U. S. Steel Corp. supplied the RJ Lee Group with steel samples for analysis. In this article, three examples of the application of this inclusion analysis approach are discussed.

Computer-controlled SEM (CCSEM) Analysis

CCSEM provides simultaneous measurement of individual inclusion size, shape (aspect ratio) and elemental composition by combining a scanning electron microscope (SEM), an x-ray analyzer and a digital scan generator under computer control. The CCSEM analyses were performed using an ASPEX Instruments "Personal SEM-2000" microscope equipped with a Gresham light element energy-dispersive spectrometer (EDS). All analyses were performed with an accelerating voltage of 20 KeV in backscattered electron imaging mode.

Inclusions were detected on the polished steel sample by moving the electron beam in discrete increments (x,y pattern) across the sample and monitoring the resultant backscattered signal to determine when the electron beam was on an inclusion. A low grid point density was used in the search mode, thereby increasing the area of the sample to be analyzed per unit time. Once a coordinate was reached where the signal was above the threshold level, the computer switched to the "acquire" mode, and the electron beam was driven across the inclusion in a preset pattern using a higher (more closely spaced) grid

point density to determine the size of the inclusion. The average, maximum and minimum diameters were recorded during the analysis.

The analysis continued until each inclusion was measured, with a < 1 second x-ray acquisition time per inclusion. At the completion of the x-ray analysis, the computer interpreted the resulting spectrum to determine which elements were present. The elements present in the spectrum were then processed to obtain their relative concentrations. Elements monitored during the CCSEM analysis included oxygen (O), sodium (Na), magnesium (Mg), aluminum (Al), silicon (Si), sulfur (S), chlorine (Cl), potassium (K), calcium (Ca), titanium (Ti), chromium (Cr), manganese (Mn) and zirconium (Zr).

Typically, from 500 to 1,000 inclusions were analyzed from each sample. This included scanning a sample area of 133 mm² at a magnification of 100X and analyzing all inclusions greater than 2 mm in size. Inclusions were grouped according to preset chemistry classifications, with their content measured both by area fraction and number density. The area fraction was further broken down into inclusions greater than and less than 10 mm in diameter. This was done to further evaluate large inclusions that can excessively inflate the area fraction measurement beyond what is statistically meaningful. The inclusion analysis process is depicted schematically in Figure 1.

Results and Discussion

Effect of Late Oxidizing Alloy Additions — Stopper rod bumps and washouts during production of Ti-stabilized ultralow-carbon (Ti-ULC) grades are known to have a strong correlation with sliver-type defects in sheet products.¹ Large washouts also have the potential to cause mold level disturbances, which can cause overflows or initiate breakouts. At U. S. Steel's Edgar Thomson Works (ETW), washouts or stopper rod bumps necessary for avoidance of excessive clogging buildups can cause slabs to be downgraded to lower-quality

Figure 2

Example of clogging behavior during casting.

applications. These downgrades are costly because there may not be sufficient orders to consume these downgraded slabs, and extra heats must be scheduled to satisfy original orders. In addition, crop losses and handling costs are associated with reprocessing the downgraded slabs. In view of the high costs in time, materials and energy usage associated with this problem, efforts were initiated in the latter part of 2001 to study this problem and determine major causes of clogging in Ti-ULC grades. A series of sampling trials were carried out at ETW with the aim of improving the understanding of factors influencing clogging behavior of Ti-ULC heats. Normal processing of these heats involves decarburization at the RH degasser facility, followed by deoxidation with aluminum and then addition of final ferroalloys such as titanium (FeTi), manganese (FeMn) and phosphorus (FeP). If the temperature is above the aim order temperature, chill scrap may also be added with the late alloys.

Samples were collected from the mold of the dual-strand caster normally three times per heat: after 130,000 pounds drained from the ladle, at approximately half of the full ladle weight and at ladle shutoff. Tundish samples used in this study were the final chemistry test, normally taken with 100,000 pounds left in the ladle. To assess clogging during production of these heats, the stopper rod behavior was analyzed, and a "clogging index" was calculated. Typical behavior when clogging is evident during casting is shown in Figure 2. This calculation was based on: (1) summation of the magnitude of stopper rod discontinu-

Figure 3

Effect of late chill scrap addition on alumina inclusion content in mold samples taken at ladle shutoff.

ities above a certain threshold associated with washouts and bumps for each heat, and (2) overall change front to back of the heat, subtracting any influence of throughput and tundish head height on stopper rod position.

As Figure 3 shows, one of the most striking observations from these trials was a very strong relationship between late chill scrap additions and alumina inclusion content in the mold samples, particularly those taken at ladle shutoff. Chill scrap has been linked in the past to increased tin can defects.² However, little else appears to have been mentioned in the literature on its effect on steel cleanliness. As Figure 4 shows, higher alumina inclusion content, as measured by automated inclusion analysis, relates strongly to the clogging seen in these heats. Further illustration of the impact of chill scrap addition on clogging is shown in Figure 2; while no chill scrap was added to Heat A, 1,500 pounds of chill scrap was added after the final Al deoxidation addition in Heat B. Therefore, it was clear that chill scrap addition was creating alumina inclusions that contributed to clogging and slab downgrades. It is believed that the oxygen source associated with chill scrap is surface oxidation ($\text{FeO}/\text{Fe}_2\text{O}_3$) due to exposure of the chill scrap to the environment. Examination of chill scrap in use at the degasser confirmed that this was the case. Addition of chill scrap to deoxidized steel results in the reduction of $\text{FeO}/\text{Fe}_2\text{O}_3$ by aluminum, as indicated in Equation 1. This creates a fine cloud of inclusions that have little opportunity for removal from the steel before entering the caster

Effect of alumina inclusion content on clogging index.

Effect of FeP addition on number density of alumina inclusions in tundish samples (heats with chill scrap additions excluded).

pouring system. In addition, the presence of titanium in steel, both as a dissolved element and as TiO_2 in alumina inclusions, is known to increase the wettability of alumina-based inclusions, which is believed to reduce the rate of inclusion flotation and removal.³

As Figures 4 and 5 indicate, a second late alloying addition, ferrophosphorus (FeP), was identified as contributing significantly to the alumina inclusion content. Phosphorus-containing grades have been associated with increased nozzle clogging⁴ and lower yield of calcium in calcium-treated grades.⁵ However, explanations for the role of phosphorus, which hinge on arguments such as competition of aluminum and phosphorus for oxygen,⁶ solidification segregation⁷ and formation of Ca_3P (which is meant to explain its effect on calcium),^{4,7} are clearly unsatisfactory. Phosphorus, as an element dissolved in steel, is not strongly surface active⁸ (hence it is likely to have little effect on inclusion flotation), and its oxide in liquid steel is less stable than FeO . The FeP in use at ETW was found to be relatively porous in appearance, which indicated that it had high ratio of exposed surface area to volume. Further examination of the material using SEM-EDS analysis indicated the presence of iron oxides ($\text{FeO}/\text{Fe}_2\text{O}_3$) and a calcium-containing phosphate scale on exposed surfaces of the material. The presence of this type of oxidation is not surprising given that, unlike other ferroalloys (e.g., FeSi , FeTi , FeMn), phosphorus is not effective in forming a protective scale to inhibit iron oxide formation, and the slag formed

in its production is calcium-rich phosphate. The mechanism for alumina inclusion generation is therefore virtually identical to that associated with chill scrap with the exception that, along with $\text{FeO}/\text{Fe}_2\text{O}_3$, the phosphate-rich scale present with this material generates alumina inclusions according to:

In light of these findings, efforts have been directed toward reducing the amount of chill scrap with the final alloys at the degasser. Where possible, chill scrap is added prior to deoxidation. Under this condition, it can have very little influence on alumina inclusion generation. The maximum acceptable ship temperature was also increased slightly. These minor practice changes, along with an increased awareness of the detrimental effect of hot heats on steel cleanliness, have significantly reduced chill scrap usage in the shop. Figure 6 shows that the reduced chill scrap additions have directly translated to fewer slab downgrades. This simple realization has allowed the single tundish sequence length for Ti-ULC grades to be increased by three heats and has contributed to improvements in submerged entry nozzle life. Additional cost savings have also been realized from simply using less chill scrap.

To reduce late FeP additions in rephosphorized grades, practices have been changed to add FeP to the tap ladle depending on phosphorus content in the steel sample taken at turndown. Since phosphorus forms no stable oxides in liquid steel at steel-making temperatures, it can be added to open (nondeoxidized) heats without any

Figure 6

Relationship between monthly average of chill scrap and number of clogging related slab downgrades.

Figure 7

Effect of late FeP additions on slivers in inspected coils (*n* refers to number of coils inspected).

major concerns related to unpredictable recovery or impact on oxygen levels in the steel. Further confirmation of the deleterious effect of late FeP additions on product quality was confirmed in the relationship between cold rolled coil slivers and late FeP additions in rephosphorized bake-hardenable grades produced at U. S. Steel's Gary Works (Figure 7). Practices in all shops are being changed accordingly to minimize late additions of FeP.

Degasser Circulation Rinse Study — At U. S. Steel's Great Lakes Works (GLW), processing time at the RH degasser has a strong influence on throughput in the shop. A savings of 2–3 minutes per heat can translate into two to three additional heats per day through the degasser and can also help reduce degasser refractory costs on a per-heat basis. Therefore, efforts have been initiated to reduce process time without reducing chemistry compliance or steel cleanliness. At the time that these efforts were initiated, Ti-ULC heats processed through the degasser had a 5-minute or 7-minute circulation rinse after final alloys were added. This practice is a measure to encourage inclusion flotation and reduce clogging and quality defects. Circulation at the degasser after deoxidation and final alloy addition have been shown to reduce inclusion content in a number of studies.^{1,9–12} However, the length of time after final alloy additions required to produce the maximum benefit is in question. Some studies seem to indicate that most benefits are achieved within the first 5 minutes of circulation, while work by Jungreithmeier et al.¹ indicates that further inclusion removal does not occur after Ti addition. There also may be a role of ladle residence time before casting that is not factored

into these considerations. The bottom line is whether circulation rinsing beyond 4–5 minutes produces a perceptible difference in inclusion content in the caster mold.

To answer this question, detailed inclusion analysis was carried out to determine the effect of the final degasser circulation rinse on steel cleanliness. At GLW, production of Ti-ULC degas grades follows a sequence similar to that at ETW, with the major difference being that the RH degassing facility has exchangeable twin vessels. At the degasser, successive steel samples were taken during the final circulation rinse phase of the operation using the automated ladle sampling system. Samples were taken approximately once per minute in the trial heats.

Results of the total oxygen and inclusion analyses of the degasser samples are shown in Figure 8. Figure 8a shows the change in total oxygen with respect to degasser circulation time. It is clear that inclusion volume decreases rapidly in the first 3 minutes after addition of final alloys (which signifies the beginning of the final circulation rinse), but after 5 minutes, further improvements in steel cleanliness are not readily apparent. The inclusion analysis data shown in Figure 8b–8d indicate the changes in inclusion content more precisely and show that most of the inclusion flotation, in particular of Al_2O_3 and $\text{MgO}\cdot\text{Al}_2\text{O}_3$ (which are two major contributors to clogging), is completed after 5 minutes of circulation following final alloy additions. Another consideration with respect to circulation time is the mixing time of late alloy additions such as Al, Ti and Mn. Chemical analysis of these samples indicated that the circulation time required to complete the chemical homogenization process is on the order of 3

Figure 8

Effect of circulation time on (a) total oxygen, (b) Al_2O_3 inclusion content, (c) $\text{MgO} \cdot \text{Al}_2\text{O}_3$ inclusion content and (d) $\text{TiO}_2 \cdot \text{Al}_2\text{O}_3$ in degasser ladle steel samples.

minutes for regular Ti-ULC grades. This “chemical homogenization” circulation time represents the minimum rinse circulation time that will be contemplated in future degas grade practices in grades with similar levels of alloy additions at GLW.

Findings from this study have been instrumental in a decision to reduce final circulation rinse time after final alloy additions at the GLW degasser to 5 minutes for grades previously calling for a 7-minute final circulation rinse. This change was initially tested on heats produced on degasser vessel No. 1. This meant that roughly half of the best practice heats had a reduced rinse in this trial period, and this enabled a statistical test to be performed on process variables, which are indicators for increased clogging at the caster. Data compiled during this trial period showed that the

reduced circulation rinse time did not adversely affect any clogging related to caster variables such as mold level fluctuation and slidegate position swings. In fact, as Table 1 shows, slightly unexpectedly, heats with increased rinse time appeared to perform worse in terms of these casting variables. Coil sliver inspection data have also shown no statistical difference in performance between heats with 5-minute and 7-minute final circulation rinse times. This indicates that further work is required to understand exactly what are the circulation rinse requirements to minimize clogging, and it indicates that other factors, such as inclusion composition (in particular the presence of $\text{TiO}_2 \cdot \text{Al}_2\text{O}_3$ -type inclusions), may play a role. Ongoing research will investigate the possibility of reducing the circulation rinse time for other, less-critical grades.

Steelmaking Factors Affecting $\text{MgO} \cdot \text{Al}_2\text{O}_3$ Spinel Inclusion Formation — Magnesium spinel ($\text{MgO} \cdot \text{Al}_2\text{O}_3$) is a combination of MgO and Al_2O_3 and is a very stable solid oxide at steelmaking temperatures. It forms by the reaction of alumina inclusions with magnesium gas or magnesium dissolved in iron. $\text{MgO} \cdot \text{Al}_2\text{O}_3$ is a solid inclusion that cannot be modified easily to a liquid inclusion using calcium, and it contributes to clogging.¹³

For spinels to form, magnesium has to be present. During oxygen or EAF steelmaking, any magnesium present is vaporized or oxidized to MgO and removed from the steel. The Mg responsible for spinels originates in ladle processing. Magnesium can be unintentionally added as an impurity in aluminum. If high-purity Al is used, this is generally not the major source of the Mg. Magnesium can also be produced by the reaction of MgO in the refractory or ladle slag with Al, producing Mg vapor:

The Mg vapor reacts directly with the Al_2O_3 inclusion or goes into solution before reaction:

The overall reaction is simply:

However, the reaction most likely takes place with Mg forming as an intermediate, since the solid-solid reaction indicated by Equation 5 would be expected to proceed extremely slowly.

Table 1

Effect of Final Circulation Rinse Time on Clogging-related Variables

Vessel	Stir time (min.)	No. of slabs	Mold level fluctuation index*	Tundish slidegate swing index*
1	5	1,562	0.8	0.7
2	7	1,132	1.0	1.0

* Index proportional to number of slabs flagged with event.

The Mg vapor can also form by the reaction of the graphite electrode in the LMF with MgO in the slag. In the vicinity of the electric arc, the temperature can exceed $2,000^\circ\text{C}$ and Equation 6 is thermodynamically favorable:

Once the Mg vapor forms, it can react by Equation 4 to produce spinel inclusions.

The potential to produce $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel inclusions increases with the pressure of Mg vapor given by Equations 3 and 6. The vapor pressure of Mg given by the reaction with Al as a function of Al content at $1,600^\circ\text{C}$ and $1,650^\circ\text{C}$ is shown in Figure 9.

The vapor pressure of Mg from reaction with the graphite electrode is given in Figure 10. Whereas the temperature at the electrode-slag interface is unknown, it should be at least $2,100\text{ K}$ ($1,827^\circ\text{C}$). Two cases are considered: (1) the reaction with MgO refractory or an MgO -saturated slag, for which the activity of MgO is unity, and (2) the reaction with a ladle slag not saturated in MgO . The vapor pressure of Mg for this reaction is about a factor of 100 greater than for the slag reaction with dissolved aluminum. This indicates that the reaction of the graphite electrode with

Figure 9

Relationship between vapor pressure of Mg as a function of dissolved Al in liquid steel reacting with MgO -saturated ladle slag.

Figure 10

Vapor pressure of Mg for $\text{MgO} + \text{C}$ reaction for MgO -saturated and 0.5 MgO activity ladle slags.

Figure 11

Effect of LMF arc time on $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel content in Gary Works mold samples.

Figure 12

Effect of slag FeO level on $\text{MgO} \cdot \text{Al}_2\text{O}_3$ spinel inclusion content.

the slag may be a major source of Mg for spinel formation.

The Mg vapor can react directly, or more likely go into solution in iron before reacting, with an alumina inclusion to produce a spinel. There is a relationship between the pressure of Mg and the equilibrium concentration of Mg in solution. This relationship is not known accurately because the solubility of Mg in iron is very low and attempts to measure it are not precise (in analyzing for Mg in solution, MgO is also included). Furthermore, equilibrium is not expected; Mg in solution will react upon contact with an alumina inclusion.

Nevertheless, the Mg vapor pressure given in Figures 9 and 10 indicate the expected trends in spinel formation. Specifically, higher Al contents and temperature and long submerged heating times in the LMF are expected to promote spinel formation.

If Mg is formed by the slag-metal or slag-carbon (electrode) reactions, it should react with any FeO or MnO in the slag. For example:

Therefore, as the (FeO + MnO) content of the slag increases, spinels are less likely to form. However, as is well known, high (FeO + MnO) contents in the slag reduce steel cleanliness by reoxidation and may make it more difficult to modify Al_2O_3 inclusions with calcium in calcium-treated heats. Therefore, there is an optimum operating window for (FeO + MnO), depending on factors such as whether the heat is calcium treated or is a surface-quality-critical grade.

Recent inclusion studies of heats processed through the LMF at Gary Works and U. S. Steel's Granite City Works support the theo-

retical expectations discussed above. Figure 11 indicates that increased LMF arc time promotes spinel inclusion formation in accordance with Equation 6. These heats, which are low-carbon aluminum-killed, are unskimmed and not slag conditioned; consequently, ladle slag FeO levels are mostly in the range of 8–15 wt %. Therefore, in these heats the spinel contents are relatively low, but still affected by heating time at the LMF. In other cases where the ladle slag is deoxidized by Al-based slag conditioners, or heats are skimmed and fluxed, the situation is somewhat more complicated due to the varying influence of Equation 7. Figure 12 shows the impact of FeO level on spinel content in liquid steel sampled from the caster mold. Decreased FeO levels, as expected, promote increased spinel inclusion content. In particular, heats that are skimmed and fluxed produce ladle slags with very low FeO levels, and this translates to high spinel inclusion contents in the liquid steel, especially after arcing at the LMF to reheat and melt the artificial flux additions. In the cases shown in Figure 12, clogging was promoted by the high spinel content to such an extent that ladles choked off before draining could be completed. In general, heats that are unskimmed non-LMF route, such as lance stir station heats with higher FeO levels, have lower spinel levels. Development of practices to minimize spinel inclusion content based on detailed inclusion analysis studies are presently part of overall efforts to improve refractory pouring system life.

Conclusion

The ASCAT is a valuable tool for identifying casting problems and enables informed decisions on steelmaking practices that improve

productivity and quality. It has helped to identify the deleterious effects of late alloy additions to degasser Ti-ULC grades, which reoxidize the steel and generate alumina inclusions that promote clogging and reduce quality. Based on these findings, steelmaking practices have been adjusted to reduce or eliminate chill scrap and FeP additions with the final alloys at the degasser. There have been related improvements in quality, reduced slab downgrades and improvements in refractory life. Detailed inclusion analysis has been an important part of understanding the effect of circulation time on inclusions after completion of alloy additions at the Great Lakes Works RH degasser. This information is crucial to the efficient utilization of valuable degasser process time that directly affects productivity through the shop. ASCAT has also helped identify steelmaking process parameters that affect $\text{MgO} \cdot \text{Al}_2\text{O}_3$ inclusion content. It is believed that control of these inclusions is an important part of reducing clogging, improving service life of caster pouring refractories and enhancing quality. Work is continuing to expand the application of detailed inclusion analysis throughout secondary steelmaking and casting. The ultimate goal of this work is to develop a system of fast turnaround inclusion analysis that will become an integral part of process monitoring in secondary metallurgy and casting processes.

Acknowledgments

The authors wish to acknowledge the U.S. Department of Energy Office of Industrial Technology (DOE Cooperative Agreement No. DE-FC07-99ID13820) for their support in this work. The authors also thank operating and quality assurance personnel from U. S. Steel's Edgar Thomson Works, Gary Works, Great Lakes Works and Granite City Works who provided samples and data used in this study. Also, the assistance of research technicians Chris Snyder, John Estocin, Tom Garvin and Ken Powers in the collection and preparation of samples is greatly appreciated.

References

1. Jungreithmeier, A.; Pissenberger, E.; Burgstaller, K.; and Mortl, J., "Production of ULC IF Steel Grades at Voest-Alpine Stahl GmbH, Linz," *ISSTech 2003 Conference Proceedings*, Iron & Steel Society, 2003, Vol. 2, pp. 227–241.
2. McFeaters, L.B., "The Effect of Process Variables on CAS-OB Steel Refining," *Steelmaking Conference Proceedings*, Vol. 76, Iron & Steel Society, 1993, pp. 465–468.
3. Basu, S.; Girase, N.U.; Choudhary, S.K.; Khan, A.J.; and Singh, J.B., "Nozzle Clogging During Slab Casting of IF and EDD Steels," *Tata Search*, 2003, pp. 253–262.
4. "Skull Session," *Iron & Steelmaker*, Vol. 26, No. 8, Aug. 1999, p. 12.
5. Cicutti, C.; Valdez, M.; Perez, T.; Ares, R.; Panelli, R.; and Petroni, J., "Optimization of Calcium Treatment to Improve Castability," *Steelmaking Conference Proceedings*, Vol. 84, Iron & Steel Society, 2001, pp. 871–882.
6. "Skull Session," *Iron & Steelmaker*, Vol. 26, No. 9, Sept. 1999, p. 78.
7. "Skull Session," *Iron & Steelmaker*, Vol. 26, No. 10, Oct. 1999, p. 65.
8. Keene, B.J., "Review of Data for the Surface Tension of Iron and Its Binary Alloys," *International Materials Reviews*, 1988, Vol. 33, No. 1, pp. 1–37.
9. Hara, Y.; Hiraoka, H.; Sorimachi, K.; and Hiwasa, S., "Reoxidation Behavior of Ultralow-Carbon Steel in the Process of Refining and Casting," *Kawasaki Steel Giho*, Vol. 25, 1993, No. 1, pp. 7–12.
10. Yamada, M.; Mori, A.; Nagahata, T.; and Ichihara, K., "Process Developments for High Cleanliness, Ultralow-carbon Steels (Kobe Steel)," *Proceedings of International Symposium on Ladle Steelmaking and Furnaces*, Canadian Institute of Mining and Metallurgy, Aug. 28–31, 1988, pp. 195–220.
11. Tanaka, H.; Kobayashi, S.; Ishizaka, A.; Tabata, Y.; and Maeda, H., "Development of Commercially 'Pure Iron' With Extra-low Inclusions at NKK Keihin Works," *Steelmaking Conference Proceedings*, Vol. 83, Iron & Steel Society, 2000, pp. 91–97.
12. Matsumo, H., "Removal Behavior of Inclusions in Molten Steel at RH Degasser," *CAMP-ISIJ*, Vol. 12, No. 4, 1999, pp. 676–677.
13. Ahlborg, K.C., "Relationship Between Ladle Furnace Slag Oxygen Potential and Contamination of Alumina Inclusions by MgO and CaO," *Clean Steel 5, Proceedings of Fifth International Conference on Clean Steel*, Hungarian Steel Association, June 1997, Vol. 1, pp. 151–156. ♦

This paper was presented at AISTech 2004 — The Iron & Steel Technology Conference and Exposition, Nashville, Tenn.

Inclusions in Aluminum-Killed Steel with Varying Calcium Additions

Kevin Ahlborg
ISG Cleveland, Inc.
3060 Eggers Avenue
Cleveland, Ohio 44105
Tel.: 216-429-7355
E-mail: kahlborg@intlsteel.com

Richard J. Fruehan
MSE Department
Carnegie Mellon University
Pittsburgh, PA 15213
Tel.: 412-268-2677
E-mail: Fruehan@cmu.edu

Michael S. Potter
RJ Lee Group, Inc.
350 Hochberg Road
Monroeville, PA 15146
Tel.: 724-325-1776
E-mail: mpotter@rjlg.com

Steven R. Badger
RJ Lee Group, Inc.
350 Hochberg Road
Monroeville, PA 15146
Tel.: 724-325-1776
E-mail: sbadger@rjlg.com

Gary S. Casuccio
RJ Lee Group, Inc.
350 Hochberg Road
Monroeville, PA 15146
Tel.: 724-325-1776
E-mail: gcasuccio@rjlg.com

Key words: Inclusion analysis, Computer Controlled scanning electron microscopy, X-ray analysis

INTRODUCTION

There is an increasing demand for cleaner steels with low inclusion contents. In addition the inclusions in the steel often must have defined properties. For example, the inclusions should be liquid or deformable. In theory, the composition and hence the properties of the inclusions can be controlled through the chemistry of the metal and slag. Controlling or modifying the types of inclusions is sometimes referred to as inclusion engineering. Despite the major advances in our knowledge of inclusion control, including models which attempt to predict the type of inclusions which will form in certain types of steel, there is currently no rapid method of accurately knowing the type, size, and number of inclusions present.

Usually a postmortem is performed on solid samples from the liquid steel, slabs, or final products using a scanning electron microscope (SEM) or conventional metallography. Among the problems with these techniques is that they are often performed long after the steel has been processed. Usually there are inclusions of varying chemistry present due to variations in local steel chemistry, re-oxidation of the steel producing non-equilibrium inclusions, and those not formed in the steel such as mold or tundish slag (exogenous inclusions). Therefore an analysis of a single or even several inclusions may not truly reflect the cleanliness of the type of inclusions present.

To overcome these problems, RJ Lee Group and a number of partners, including several steel companies, with a grant from the Department of Energy, are developing an Automated Steel Cleanliness Analysis Tool (ASCAT). ASCAT is being designed around a computer-controlled scanning electron microscope (CCSEM) capable of taking a metal sample, performing a “just good enough” preparation and analyzing up to several hundred inclusions in less than one hour. The CCSEM generates an enormous quantity of data on inclusions including size, chemistry and morphology. One of the tasks of the overall project is to rapidly analyze the data using expert systems and neural networks to display the results in a clean simple manner which will indicate to the metallurgist or operator if the steel and/or process is satisfactory. The operator can then use this information to possibly correct the heat, prevent the problem in subsequent heats, and determine if it is necessary to downgrade the heat before costly downstream processing. To accomplish this task, the team is examining a wide range of metallurgic issues on problems concerning inclusions. For example, overall steel cleanliness through the process, calcium treatment of aluminum-killed steels, titanium oxide (TiO_x) in alumina (Al_2O_3) inclusions, obtaining deformable inclusions and the formation of Mg-spinels (MgAl_2O) are being investigated.

One of the major efforts in this study has been with LTV Steel to examine the calcium treatment of various grades of aluminum-killed steel. This paper will discuss the fundamental metallurgy, the steel processing, the CCSEM analysis, and results. How the ASCAT will work in practice for these steel grades will also be discussed.

FUNDAMENTAL METALLURGY

Calcium is highly reactive and when added to liquid steel can simply vaporize, react with oxygen, react with sulfur or modify inclusions in the steel. It is added to aluminum-killed steels for a variety of reasons; the major reason being to modify or convert Al_2O_3 inclusions into calcium aluminates. As shown in Figure [1], CaO and

Al_2O_3 can form a number of solid and liquid inclusions at steelmaking temperatures around 1600°C (1878°K). Ideally, liquid inclusions are desirable since they will not adhere to refractory surfaces causing casting nozzles to clog. These inclusions can also absorb sulfur, reducing the amount of manganese sulfide (MnS) present in low sulfur steels. Manganese Sulfide can lead to hydrogen induced cracking or brittle fracture.

It has been clearly demonstrated that in order to modify Al_2O_3 -rich inclusions to those with CaO , the sulfur content must be low, or the added calcium will simply react with sulfur forming CaS [1-2]. The equilibrium for the following reaction can be used to determine if CaS forms and to what extent the Al_2O_3 inclusion will be modified.

The parenthesis in the equation indicates it is in the inclusion while the underlined species are dissolved in the metal. To form a given type of the inclusion containing CaO , there is a critical sulfur level for a given aluminum content. For example, to form completely liquid inclusions at 1873°K and 0.03% aluminum, the sulfur content must be below about 0.008%. When the liquid inclusions solidify, they form $12 \text{CaO} \cdot 7 \text{Al}_2\text{O}_3$ or C_{12}A_7 . To form inclusions with lower CaO such as solid $\text{CaO} \cdot \text{Al}_2\text{O}_3$ (CA) the allowable sulfur level is higher. If calcium is added to steel with sulfur above the critical level, it will react with sulfur forming CaS . The lower the temperature or higher the aluminum content, the lower the critical sulfur content.

When examining the inclusions in a calcium-treated steel, they are usually complex duplex inclusions containing an oxide phase and CaS . The CaS may form by direct reaction with sulfur or precipitate from liquid oxide inclusions during solidification. The SEM gives the average composition of the entire inclusion; therefore, it is necessary to develop techniques to separate the calcium in the sulfide from the calcium in the oxide in order to identify the oxide phase.

One technique developed is to plot the inclusion composition on a calcium aluminum sulfur (Ca-Al-S) ternary diagram in mole percent. The SEM cannot accurately analyze for oxygen but does indicate the inclusion is an oxide. Therefore, if the inclusion is identified as an oxide, the oxygen is deleted and if $\text{Al}+\text{Ca}+\text{S} > 90\%$, the rest of the other elements are deleted and the three components are normalized to total 100%. An example of such a diagram is shown in Figure 2.

If there is no sulfur present, the oxide is located on the Al-Ca binary line. For example, if the inclusion is $\text{CaO} \cdot \text{Al}_2\text{O}_3$ (CA), it will be at 33 atomic % calcium. If it is in the middle of the liquid range, it will solidify as $12 \text{CaO} \cdot 7 \text{Al}_2\text{O}_3$ (C_{12}A_7) and be at 46 atomic % calcium. If the inclusion is only CaS , it will be plotted on the Ca-S binary at 50 atomic % Calcium.

The duplex or complex inclusions will consist of CaS and $\text{Al}_2\text{O}_3\text{-CaO}$ inclusion and be located in the middle of the diagram. The oxide portion of the complex inclusion can be identified by drawing the line between CaS on the Ca-S binary to the oxide inclusion on the Ca-Al binary. For example, the region of liquid oxide inclusions is in the area indicated in Figure 2. For solid $\text{CaO} \cdot \text{Al}_2\text{O}_3$ (CA) and CaS , the inclusion composition will be on

the indicated line. The region between the liquid area and the $\text{CaO} \cdot \text{Al}_2\text{O}_3$ -CaS line will represent a mixture of the $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and liquid oxide inclusions plus CaS.

Solid Al_2O_3 , $\text{CaO} \cdot 2 \text{Al}_2\text{O}_3$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3$ will clog casting nozzles. In theory, any inclusion not in the triangular area indicated in Figure 2 can cause clogging. However, it is difficult to determine when the CaS forms. It could form by direct reaction of calcium with sulfur in the melt and be in the liquid steel during processing. Calcium sulfide can also form by precipitation of sulfur dissolved in a liquid oxide inclusion. However, the solubility of sulfur is low, typically about 3 atomic percent; therefore the region for CaS precipitation is small. Calcium sulfide could also form during solidification of the steel in the caster. As the steel solidifies and the melt is enriched in aluminum and sulfur, the temperature decreases causing the reverse of reaction (1) forming more Al_2O_3 in the inclusion and CaS. This will not happen in samples taken from the melt because solidification is too rapid.

If CaS is considered, the windows for the total inclusion to be 100% and 50% liquid are shown in Figure (3). The amount of solid in an inclusion and the relative effects of CaS and solid oxide inclusions on clogging is not known. For the present case, the 50% window is arbitrarily used to indicate the potential of clogging. Other inclusions such as solid MgAl_2O_4 spinels can cause clogging and are reported. The potential of clogging is not only related to the composition of the inclusions but also the amount. The amount of 50% solid inclusions in terms of area fraction is therefore reported.

STEEL PROCESSING

The steel that was sampled for this trial was calcium treated for the purpose of shape-modifying its contained inclusions. Prior to this trial the steel was being treated with CaSi-cored wire. For various reasons LTV-Cleveland wanted to try powder injection for this product.

The steel was melted via the conventional BOF process. Low sulfur charge materials resulted in tap sulfur levels of between 0.006 and 0.009%. Manganese, silicon, coke, and a small amount of aluminum were added to the ladle during tap, along with a lime-based synthetic slag. Calcium carbide was added to the ladle after tap to condition the ladle slag.

At the LMF the oxygen potential of the ladle slag was measured with a slag probe. Based on the probe reading, the slag was deoxidized further with an addition of lime-32% Al. Afterward the first LF steel sample was obtained. The analysis of the LF1 sample determined the subsequent alloy trim additions.

Once the steel chemistry was trimmed, the steel was injected with CaSi powder. The trial was designed to identify the optimal CaSi powder addition needed for this grade. The first heat was treated with 600 pounds CaSi, 20% less than was normally added via CaSi wire. The ladle analysis indicated that the residual Ca level was higher than desired, so for each of the next 8 heats the CaSi dose was reduced in increments of 50 to 100 pounds.

The steel was sampled numerous times in the ladle during processing, including:

- after tap,
- just prior to CaSi treatment,
- just after adding CaSi,
- a final ladle test,
- in the tundish, and
- from the hot band product.

The samplers used for this trial were the standard lollipop-type and did not contain any deoxidant, so that inclusions in the samples would be representative of the process.

COMPUTER-CONTROLLED SEM ANALYSIS

The CCSEM analyses were performed using an ASPEX Instruments "Personal SEM-75" microscope equipped with a Gresham light element energy dispersive spectrometer (EDS). In addition, all analyses were performed with an accelerating voltage of 20 KeV in backscattered electron imaging mode.

Computer controlled scanning electron microscopy provides simultaneous measurement of individual inclusion size, shape (aspect ratio) and elemental composition by combining a scanning electron microscope (SEM), an x-ray analyzer (EDS), and a digital scan generator under computer control. Use of the computer to control the analysis permits large numbers of individual inclusions to be analyzed in a time efficient manner.

The CCSEM analysis was performed using the backscattered electron signal to create the viewing image, which sensitive to atomic number. In this study, the threshold for inclusion detection was set such that inclusions were easily detected in the steel matrix and measured during the CCSEM analysis.

During the CCSEM analysis, fields on the samples were analyzed "in order". Inclusions were detected on the polished steel by moving the electron beam in discrete increments ("x, y" pattern) across the sample and monitoring the resultant backscattered signal to determine when the electron beam was on an inclusion. At each point, the computer directed the electron beam to pause while the image intensity was compared to the preset threshold level. This comparison was used to determine whether the electron beam was "on" an inclusion (i.e., above the preset intensity threshold) or "off" an inclusion (i.e., below threshold). If the signal was below the threshold level, the computer directed the digital scan generator to move the electron beam to a new (x, y) coordinate. This point-by-point approach permitted the CCSEM analysis to be performed using "search" and

"acquire" modes. A low grid-point density was used in the search mode, thereby increasing the area of the sample to be analyzed per unit time. Once a coordinate was reached where the signal was above the threshold level, the computer switched to the acquire mode and the electron beam was driven across the inclusion in a preset pattern using a higher (more closely spaced) grid point density to determine the size of the inclusion. The average, maximum and minimum diameters were recorded during the analysis.

Upon measurement of the inclusion size, the elemental composition of the inclusion was determined through collection of characteristic X-rays that were generated when the electron beam was on the inclusion. In this study, the X-ray acquisition continued until each inclusion achieved a 0.45 second acquisition (~1200 X-ray counts). At the completion of the X-ray analysis, the computer interpreted the resultant spectrum to determine which elements were present. The elements present in the spectrum were then processed to obtain their relative concentrations. Elements monitored during the CCSEM analysis included oxygen (O), magnesium (Mg), aluminum (Al), silicon (Si), sulfur (S), chlorine (Cl), potassium (K), calcium (Ca), titanium (Ti), chromium (Cr), and manganese (Mn). A density was assigned to each inclusion based on its elemental composition.

Approximately 325 to 1500 inclusions were analyzed from each sample. This included scanning the a sample area of 133 mm² at a magnification of 100X for all inclusions greater than 2 µm.

RESULTS AND DISCUSSION

In a series of seven heats, the amount of CaSi (30% calcium) added varied from 114 to 274 kg per heat or 0.46 to 1.12 kg of CaSi per ton. The steel had lower aluminum contents than for normal aluminum-killed heats, 0.015 to 0.020%. The steel was desulfurized to 0.004 to 0.009%. In all cases, the sulfur content was below that necessary to ensure liquid calcium aluminates should form. The heats were conducted to determine the optimum amount of CaSi required. If there is insufficient calcium, not all of the inclusions will be completely modified to liquid inclusions. On the other hand, if there is too much calcium, CaO-rich inclusions may form causing nozzle erosion or excessive CaS may form which can clog the nozzle.

The ASCAT analyzed all of the inclusions in the steel samples and separate out the oxides and CaS from the other sulfides, primarily MnS. There would typically be 50 to 300 oxide inclusions primarily containing calcium, aluminum, and sulfur. The chemical composition and sizes of the inclusions are indicated on a Ca-Al-S ternary diagram along with the 50% and 100% liquid inclusion ranges. Also included in the summary sheet is the Ca/Al ratio, total area of oxide inclusions, composition distribution for inclusions with less than 10 atomic percent sulfur, the area of Mg spinels and if there is mold or tundish slag present.

Typical results when using 114 kg and 274 kg of CaSi per heat are shown in Figures 4-7. Also indicated in Figure 4, other information including the amount of spinels present, if there is any indication of any flux or slag, and the area fraction of liquid inclusions. Prior to the CaSi addition, the inclusions were primarily Al₂O₃ in all cases, typically 10 to 50 mm in size. The composition and sizes of the inclusions from a ladle sample are shown in Figure 4. The inclusions have been converted to liquid calcium aluminates with some CaS. In general, the inclusions are smaller than prior to the CaSi addition. The area fraction of oxides decreased from 700 ppm to 90 ppm, but the area fraction of CaS increased from 2 ppm to 20 ppm. The composition for a sample from the tundish is shown in Figure 5. The composition and area fractions did not change significantly.

The inclusion composition band became tighter and there was some inclusion agglomeration. The amount of inclusions, which was over 50% solid, was 28%. Samples from the hot band were also taken; these will be discussed later.

For the heat in which 274 kg (1.12 kg/t) of CaSi was added, the inclusion composition and sizes for the ladle sample are shown in Figure 6. In this case, the inclusions contain large amounts of CaS and the oxide portion is rich in CaO, most likely liquid plus CaO at steel making temperatures. The area fraction of oxide inclusions is similar to that for the lower addition, but the CaS area is much greater. The results for the tundish sample are shown in Figure 7. The inclusions are better defined but still contain large amounts of CaS, and the oxide portions are CaO-rich. The percentage of inclusions which are 50% solid is over 90%.

Similar results were observed for the other amounts of CaSi additions. There was no significant difference in the area fraction of oxides which would be related to the total oxygen content. However, there was a significant difference in the area of inclusions less than 50% liquid which includes CaS. As more CaSi is added, there are more predominantly solid inclusions as shown in Figure 8. This means it is possible to add too much calcium to prevent clogging. The inclusions become very rich in CaS and CaO and a large number are more than 50% solid as the amount of CaSi addition increases. In this case, about 130 to 150 kg of CaSi, or 0.6 kg/ton appears to be optimum for obtaining liquid inclusions. Since calcium is the important reactant, this represents only 0.18 kg of calcium per ton of steel.

Samples were also collected from the hot band. It is important to note that inclusion composition from the product can differ from the ladle and tundish. Samples from the ladle and tundish are quenched while the product is relatively slow cooled. As the steel solidifies in the slab or bloom, inclusions may be engulfed into the steel as it solidifies at the solidification front. In general, the rate of solidification is slow, and the inclusions are pushed into the remaining liquid. This phenomena has been recently investigated by Wang et al³. using a laser confocal microscope in which they observed the inclusions during solidification. The solute elements, in particular aluminum and sulfur, are rejected from the solid into the liquid during solidification. In addition, the temperature is lower, about 1520°C, as compared to that in the ladle or tundish (1600°C). The increase in aluminum and sulfur and the lower temperature causes reaction (1) to shift to the left, forming more Al₂O₃-rich inclusions and CaS.

The inclusion compositions in the hot band for 114 kg and 275 kg CaSi additions are shown in Figures 9 and 10. As compared to Figures 5 and 7, it is clearly evident that the inclusions become more Al₂O₃-rich. A similar behavior was observed for other amounts of CaSi additions. In most cases, there was also an increase in the amount of CaS. It could be argued that the shift to Al₂O₃-rich inclusions resulted from reoxidation of the oxide. However, there was no evidence of reoxidation; the total oxygen did not increase and the total area of oxide inclusions did not increase.

POTENTIAL USE OF ASCAT AND CONCLUSIONS

The use of ASCAT as a process development and research tool has been demonstrated in this paper. In this case, ASCAT was used to identify the inclusions present in the steel, determine the optimum CaSi addition, and shows how the inclusions change during solidification.

However, the ultimate goal is to use ASCAT as a production tool. For the present example, if the information is available quickly, actions regarding the heat can be made. The general characteristics of the inclusions are known from the first ladle sample as seen in Figures 4 and 6. If the inclusions are on the right side of the ternary phase diagram (Al_2O_3 -rich region), more CaSi could be added. If the inclusions are to the left side of the ternary phase diagram, or are high in CaS, it may be possible to add oxygen to oxidize the inclusions forming liquid calcium aluminates and reducing the amount of CaS. This practice may be difficult to control and would need to be developed.

The tundish samples give more precise information. Whereas it is too late to correct the heat, the information can be used to modify subsequent metallurgical practices. The ASCAT will also give information as to how the slab will be processed or distributed. If a heat of steel has too many or the wrong type of inclusions, it may be diverted to a less critical grade.

In addition to demonstrating the use of ASCAT, the present work indicates the optimum of amount of CaSi required. For the conditions presented in this study, 0.6 kg/ton of CaSi or 0.18 kg/ton of calcium produced the desired inclusions. Excessive amounts of CaSi could lead to a large quantity of CaS even for low sulfur steels and CaO-rich solid inclusions or liquid inclusions high in CaO which can cause erosion of the nozzles. The present work also shows that the inclusions in the hot band and the slab can be significantly different than these in the liquid steel. The inclusions tend to become more Al_2O_3 -rich due to segregation of aluminum and sulfur during solidification and the lower temperature.

ACKNOWLEDGEMENTS

The authors wish to thank the US Department of Energy (award No. DE-FC07-99ID13820) for the financial assistance provided to allow for this study.

REFERENCES

1. *The Making, Shaping, and Treating of Steel, Steelmaking and Refining Volume*; Fruehan, R. J., Ed.; AISE Steel Foundation: Pittsburgh, PA 1998.
2. Larsen, K., Fruehan, R. J.; Trans ISS, I&SM, pg. 45, July 1990.
3. Wang et al

Figure 1 Binary Phase Diagram: CaO and Al₂O₃

Figure 2 Schematic diagram including regions for 100% liquid oxides (shaded region) and 50% liquid (entire region)

Figure 3 Schematic diagram indicating region in which the entire inclusion including sulfides is 100% (shaded region) and 50% liquid.

Ladle Sample: CaSi addition = 114 kg

Figure 4 Inclusion composition and sizes plotted on a Ca-Al-S ternary phase diagram in a sample from the ladle after 114 kg addition of CaSi.

Tundish Sample: CaSi addition = 114 kg

Figure 5 Inclusion composition and sizes plotted on a Ca-Al-S ternary phase diagram in a sample from the tundish after 114 kg addition of CaSi.

Ladle Sample: CaSi addition = 275 kg

Figure 6 Inclusion composition and sizes plotted on a Ca-Al-S ternary phase diagram in a sample from the ladle after 275 kg addition of CaSi.

Tundish Sample: CaSi addition = 275 kg

Figure 7 Inclusion composition and sizes plotted on a Ca-Al-S ternary phase diagram in a sample from the tundish after 275 kg addition of CaSi.

Figure 8 Area Fraction of oxides which are all liquid, 50-100% liquid, and less than 50% liquid as a function of the amount of CaSi

Hot Band Sample: CaSi addition = 114 kg

Figure 9 Inclusion composition and sizes plotted on a Ca-Al-S ternary phase diagram in a sample from the hot band after 114 kg addition of CaSi.

Hot Band Sample: CaSi addition = 275 kg

Figure 10 Inclusion composition and sizes plotted on a Ca-Al-S ternary phase diagram in a sample from the hot band after 275 kg addition of CaSi.