

Future Demands on Ferroalloys from the Customers in the Steel Industry

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ABSTRACT

Within the steel industry an increased knowledge of how size, distribution and composition of inclusions change during steelmaking has been gained during the recent years. Some of the reasons for this will be discussed in the paper. One example is a new method (OES) for on-line determination of micro inclusion characteristics that has been developed by Ovako Steel. This enable, for the first time, the steel producers to follow the change in micro inclusion characteristics during steel making. Another example is a new method for determining macro inclusions during steelmaking. The method is named Liquid Sampling and Hot Rolling (LSHR), after the procedure of preparing the samples before analysis. Here, immersed ultrasonic testing is used to determine the macro inclusion content in the samples. The effect of this new knowledge on the demands on ferroalloys is discussed. One possible scenario is that specifications on inclusion characteristics in ferroalloys will be a requirement from the steel producers focusing on clean steel. Thus, specifications on average size, shape, quantity and composition might be added to the existing specifications on dissolved element content in ferroalloys. Another scenario is that new ferroalloy products will be needed in the steel industry. Examples of such products will be discussed.

1. INTRODUCTION

Recently new techniques for determination of inclusion characteristics have been developed in the steel industry. These will give the steelmakers tools which can help them to optimize the inclusion characteristics so it is appropriate for each steel grade and results in desired material properties.

Today, it is not possible to control the micro-inclusion characteristics during ladle refining using traditional methods, when adding, for example, ferroalloys to the steel. This is more obvious if one studies the example in **Table I**. Here the three quality parameters that are used for control in the production of "clean steel" are compared throughout the process.

The first quality parameter is the content of elements dissolved in the liquid steel. These are alloying elements such as Si, Mn, Cr, etc. and impurities such as S, H, P, Cu, etc. These contents are relatively simple to determine by taking a ladle, tundish or mold sample followed by chemical analysis. Usually, an analysis can be ready within 7 to 10 minutes from sampling.

Thus, the operator has a chance to make adjustments during liquid steel treatment in the ladle. After the steel is solidified the chemical composition does not usually change much and further process control is unnecessary. The second quality parameter is temperature. This can easily be determined with a rapid response time during liquid steel treatment and metalworking. Thus, temperature can also be controlled throughout the process. The third quality parameter pertains to inclusions characteristics. This includes total oxygen content, composition and size. Based on size, inclusions are also normally categorized as micro-inclusions (here defined as smaller than 22 μm) and macro-inclusions ($>22 \mu\text{m}$). For the majority of steel companies, rapid feedback of inclusion characteristics during liquid steel making is not available and steel cleanliness can therefore not be controlled with respect to inclusion content. The total oxygen content, composition and size are normally determined using melt extraction, scanning electron microscopy (SEM) combined with energy disperse spectroscopy (EDS), and light optical microscopy (LOM) and classification according to a standard such as SS111116 (JK II)¹,

respectively. None of these methods are able to provide a rapid enough feedback to the process so that the information can be used for on-line monitoring or control of the process. However, recently one company, Ovako Steel AB, has reported²⁻⁴ that they are currently testing a modified OES (optical emission spectroscopy) method for on-line determination of micro-inclusion size distribution. This method is also currently studied by other research groups around the world and will probably also be tested in other steel plants in the near future.

	Ladle	Tundish	Mold	Metal working
Elements that dissolve in steel	yes	yes	yes	yes, not necessary
Temp.	yes	yes	yes	yes
Micro and macro inclusions	no	no	no	yes, off-line

Table 1. Possibilities to control steel quality parameters during production.

As steelmakers are able to, for the first time, get on-line information regarding inclusion characteristics, new demands on ferroalloys will be created. This paper will discuss possible scenarios. The first part of the paper gives more detailed information regarding the new developments to achieve new information on inclusion characteristics, which have taken place in the steelmaking community. Thereafter, the effect of these new developments on the demands on ferroalloys and the ferroalloy producers are discussed.

2. DEVELOPMENTS IN THE STEEL INDUSTRY

Steel is made in either an integrated steelmaking route or a scrap-based route, where the raw material is iron ore and scrap, respectively. However, the finished products in both cases have the same strict demands on material properties, which, of course, varies with application. The inclusion characteristics has major impact on the material properties and is therefore very important to control. In general

the larger the inclusion the more harmful effect on the material properties. Thus, macro inclusions are more important to remove from the steel than micro inclusions.

So far the control is done on finished material from the metal working mill. The total oxygen content and size distribution are analyzed on a regular basis using melt extraction and LOM, respectively. Often also the inclusion compositions are determined using SEM combined with EDS. Most companies with strict customer demands on material properties have carried out these inclusion determinations for decades. Thus, a large amount of information has been gathered. This is also used to optimize the steelmaking process before casting when steel is in liquid state. However, this is difficult to do with a great accuracy since no information is available during the steelmaking. Therefore, steelmakers carry out special investigations where samples are taken during different parts of the process and thereafter the inclusion characteristics is determined.⁵⁻⁷ This does not provide on-line information, since the determination of the inclusion characteristics for a single heat may take weeks. However, it is the best approach available today for most steelmakers.

2.1 Micro Inclusion Characteristics

It represents a minor revolution in steelmaking when a method for determination of micro inclusion characteristics is being tested on-line today during steelmaking. The method being tested is the spark-induced optical emission spectroscopy (OES) method and it is developed at Ovako Steel.^{2,3} The principle is shown in **Figure 1**. A steel sample, taken in liquid steel (or in finished material) is hit by an electric discharge. This creates light intensities, which are divided by a grating into respective wavelength and detected by separate units for each element (Al, Mg, Ca, etc). From this information it is possible to determine the total oxygen content, size distribution and composition of inclusions. At the same time, it is possible to determine the dissolved element contents.

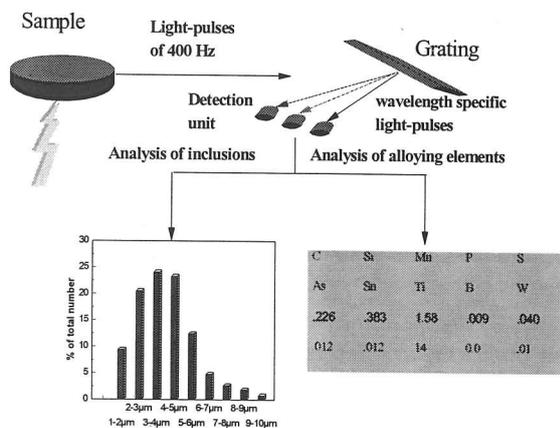


Figure 1 The basic principles of the OES method.

In order to show the usefulness of the method some examples will be given. **Figure 2** shows the change in micro inclusion content during the following four production steps: i) at the ladles arrival to the ASEA-SKF ladle furnace, ii) before vacuum degassing (after alloying), iii) after vacuum degassing, and iv) at the end of the ladle treatment. As can be seen, the number of inclusions of all sizes decreases from the beginning of the ladle treatment to after vacuum degassing. After vacuum degassing almost no inclusions larger than 6 μm are left in the steel and during the final treatment period the size distribution stays almost the same.

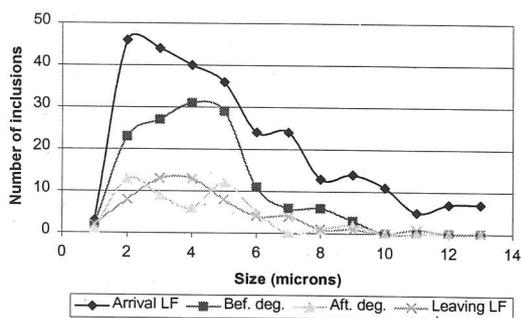


Figure 2. The number of inclusions in samples taken during different parts of the ladle refining operation.⁷

Figure 3 shows the inclusion composition in steel samples taken after deoxidation and alloy addition but before vacuum degassing. The steel grade is an aluminum-deoxidized bearing steel. The inclusions were sorted into the following groups: i) alumina inclusions (A) with at least

95% Al_2O_3 , ii) alumina inclusions with MgO (M-A), iii) alumina inclusions with CaO (C-A), and iv) alumina inclusions with both CaO and MgO (C-M-A). From the information it can be concluded that the majority of the inclusions are pure alumina inclusions, which most likely derive from the deoxidation process. The complex inclusion containing MgO and CaO might derive as a result of the alloy with addition or due to reactions with slag.

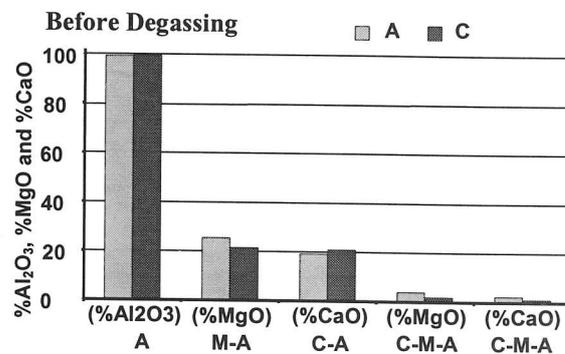


Figure 3. Average composition of different types of inclusions found before vacuum degassing⁸

Currently, the Ovako OES method can only be used for determination of inclusions up to a size of approximately 13 μm and it does not account for the Si content in the inclusions. It also requires special rapid solidifying sampler. Still, it represents a major step forward in obtaining on-line information regarding inclusion characteristics. It has a great future potential for improving the steel process so the optimum steel can be produced to assure the desired material properties for each customer.

2.2 Macro Inclusion Characteristics

As mentioned earlier, macro inclusions are in general more harmful to material properties than micro inclusions. Therefore, it is very important to decrease the number of macro inclusions during steelmaking. One problem is that currently no methods exist to obtain on-line information of macro inclusions. Another problem is that the number of macro inclusions in steel grades of high cleanliness is very small. However, the few remaining can still be very harmful to the material properties for steel

products with high demands on performance. These macro inclusions are very difficult to find in the LOM, because of the relatively small sample areas (i.e. 200 mm²). It is also very unlikely that an inclusion is cut exactly in the middle when preparing the sample for microscopic analysis. The classification of macro inclusions according to the SS111116, P-type inclusions larger than 22.4 μm, can account for these difficulties if more than 30 inclusions are found. Then the effect of section on the determination of the size distribution of macro inclusions is less pronounced. Therefore, it is necessary to analyze a large enough sample

area, which requires a larger sample volume. Analyzes of macro inclusions in clean steel therefore becomes very time consuming.

For the above reasons the liquid sampling and hot rolling (LSHR) method has been developed.^{9,10} It is illustrated in **Figure 4**. A special sampler with the dimensions 150x25x15 mm has been developed. This can be used for sampling in the ladle, tundish or mold. The sample pin can be used for total oxygen analysis. The bar can be used for determination of macro as well as micro inclusion size and compositions. A new development is the analysis of the macro inclusion sizes using an immersed ultrasonic scanning (US) technique combined with a high frequency detector. This requires a careful sample preparation as illustrated in **Figure 4**, including deformation of the sample by rolling. A step that illustrates an advantage with the method. It is possible to deform the sample at the same temperature and reduction degree as for standard samples normally taken in the rolling mill. Thus, a more realistic comparison of the inclusion morphology between samples taken in liquid steel and finished material can be done.

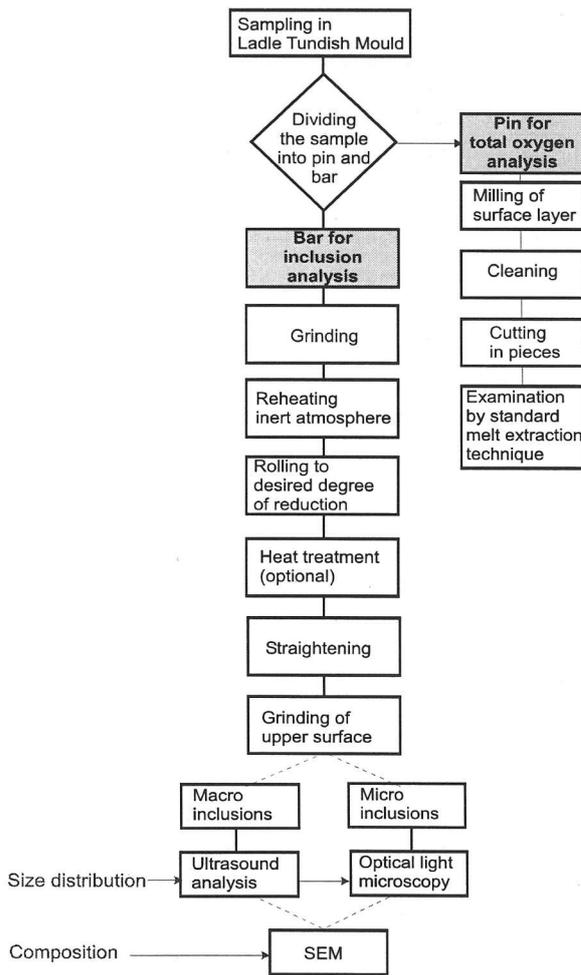


Figure 4. The Flowchart describing the LSHR method.

Figure 5 shows an ultrasonic scanning picture of a rolled LSHR sample, which has been taken before vacuum degassing. The grade is bearing steel of high cleanness. The sample size is 26 x 50 mm and the inspected zone depth is 1.3 mm in the center part of the sample. The color corresponding to 100% in the figure has been set by calibration using a measurement on a 200 μm hole, which has been drilled in a calibration steel sample. Thus, the typical inclusion found in the picture is about 30-40 μm. It is also obvious from the figure that the sample edges give rise to unrealistic indications of inclusions. It should also be pointed out that the number of macro inclusions in the steel sample is very small, which should be expected in a bearing steel at this stage of the refining operation.

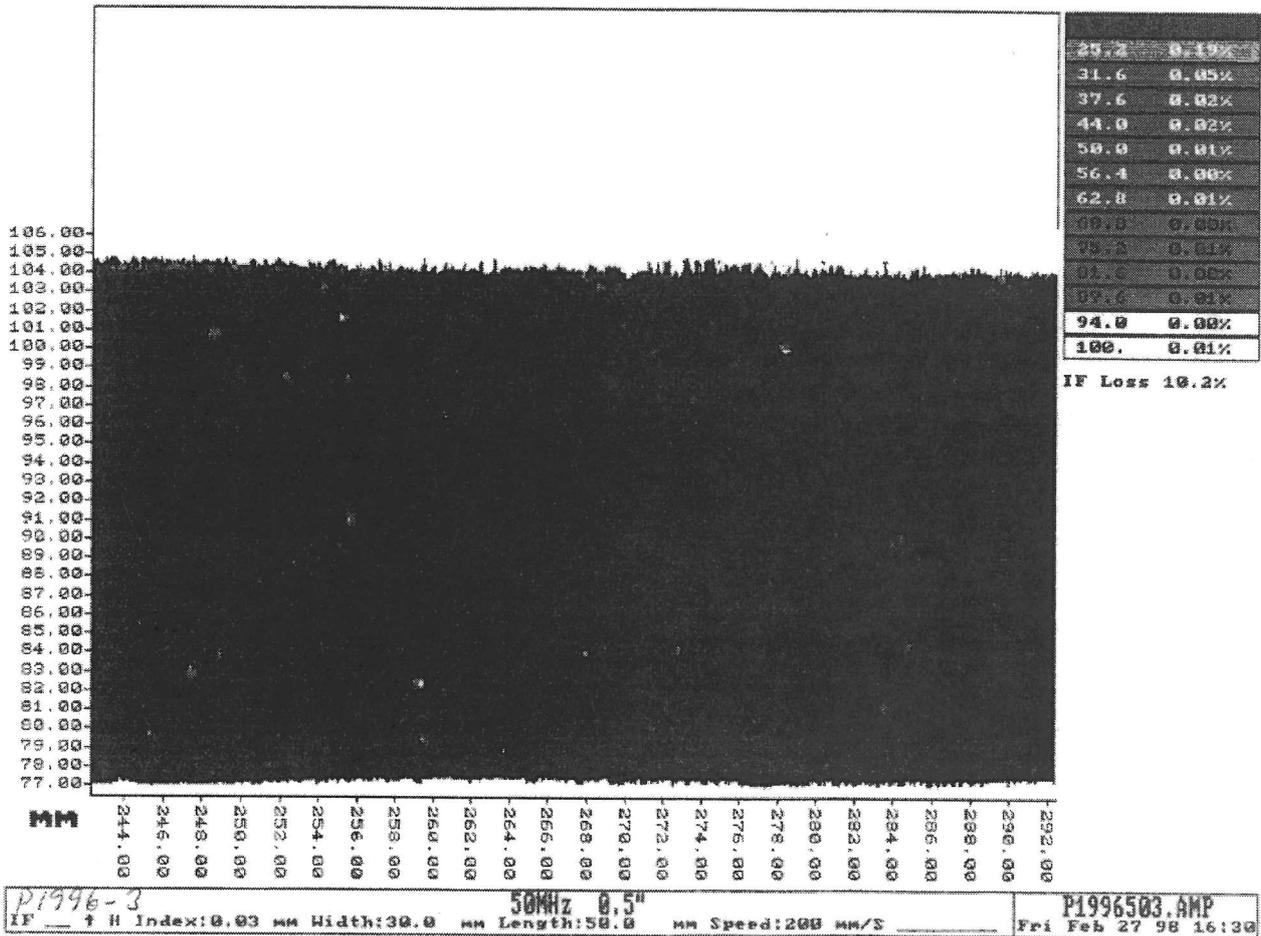


Figure 5. Example of ultrasonic scanning of a rolled LSHR sample.¹⁰

The use of the LSHR methodology in combination with immersed ultrasonic scanning provides new information as compared to when determining inclusions using LOM. Tests showed that no inclusions larger than 25 μm could be found using LOM, despite looking for hours. However, rather than seeing LSHR in combination with US analysis as a competitive method to LOM and OES, it should be seen as a complement. This is illustrated in Figure 6. The number of inclusions per unit volume is plotted versus the inclusion size. The inclusions smaller than 45 μm were analysed by LOM and classified according to SS111116 and the larger inclusions with US. The steel samples were taken at three different stages of the refining process. Thus, the figure illustrates that it is possible to receive information on both the micro and macro inclusion characteristics during ladle refining.

Finally, it should be once more stressed that the LSHR method in combination with the US does not provide on-line information of macro inclusion sizes. However, as today it is the best that is available. It can be used for some process optimization.

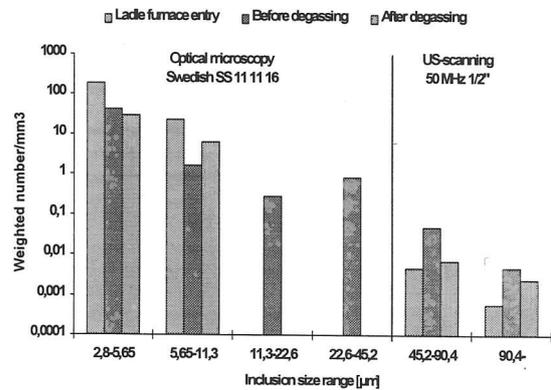


Figure 6. Comparison of results of inclusion determination using LOM and US.¹⁰

3. DEMANDS ON THE FERROALLOY INDUSTRY

The discussion of future demands on ferroalloys is partly based on information gathered in discussions with representants from the steelmaking community in August 1996¹¹ and May 2000.

3.1 Today

During the discussions with the personnel at the steelworks the following general demands on ferroalloy producers were suggested:

1. More comprehensive analysis of dissolved elements in ferroalloys. Today, information often is lacking especially with respect to impurity and trace elements such as P and Sb, Sn, Pb and Bi, respectively.
2. Help with optimisation of the storage and handling systems of ferroalloys at each steelworks. This is necessary, for example, to avoid problems of increased moisture in the ferroalloys during production stops.
3. Information on inclusion characteristics of the ferroalloys.

There are also additional demands on the ferroalloy suppliers, which are more specific for certain steel grades. In general, it is advantageous to have low or well known contents of strong deoxidizers such as Al, Ca, Mg and Ce. It is also necessary to have low contents of Si in steels where aluminium is the deoxidiser and low amounts of Al in steels where silicon is used as deoxidiser. The content of Ti in ferroalloys should also be kept low for most steel grades, since Ti will react with C and N and form hard carbo-nitrides that will negatively affect material properties such as fatigue in the finished steel. The P content should also be kept low since it has a tendency to migrate to the grain boundaries, which makes the steel brittle.

3.2 The Ferroalloy Industries Efforts

In many cases the ferroalloy suppliers meet the first two demands in section 3.1. Information regarding trace and impurity elements are

supplied in connection with delivery of the product or on demand. There are also some cases where steel companies have received help to optimize the storage and handling systems. However, due to cut down on personnel in the steel companies it is very likely that suppliers of, for example, ferroalloys will have to provide the knowledge of how to handle the ferroalloys in the future.

The ferroalloy producers have also studied the inclusion characteristics for some ferroalloys. A review of the open literature showed that total oxygen content, size distribution and composition of inclusions have been reported for some ferroalloys, **Table 2**. These studies have been carried out to determine the inclusion characteristics in a particular ferroalloy grade or compare the inclusion characteristics in different steel grades. Also, the majority of the studies have been focused on determining the inclusion compositions in ferroalloys. Very few investigations have been aimed at providing information on inclusion size distributions.

	Otot	Size	Composition
FeCr	12, 13	14, 15	12, 14, 16, 13, 17, 18, 19
FeMn	20, 21	20, 21	19, 20, 21, 22
FeMo			19
FeSi	23, 24		23, 24, 19
FeTi			19, 25
SiMn			26

Table 2. References to literature about inclusion characteristics in ferroalloys.

One example of a size distribution is shown in **Figure 7**. The area fraction of inclusions in steel samples are plotted as a function of the carbon content in the ferroalloy. The results are for laboratory experiments carried out in a 20 kg scale. It is seen that the fraction of inclusions in the steel decreases with an increased carbon content in the added FeMn-alloy. Additional determinations of the inclusion characteristics in the different FeMn alloys showed that the inclusion fraction also decreased with an increased carbon content in the alloy. Thus, the higher inclusion content in the low-carbon FeMn also resulted in a higher inclusion content in the steel.

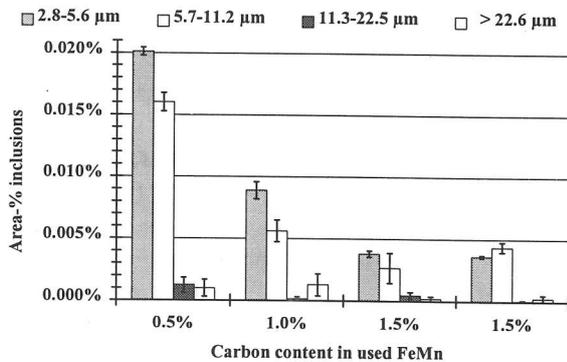


Figure 7. The effect of carbon content in FeMn on inclusion content²⁰.

Another example of determined size distributions in ferroalloys is shown in **Figure 8**. Here, the average area-% of inclusions in tool steels for plastic applications is shown for a granulated, standard and a high purity FeSi grade. The high purity FeSi grade contains < 0.03 %Al, 0.04 %Ca, and <0.03 %Ti and the standard FeSi grade contains less than 1.5 %Al.²³

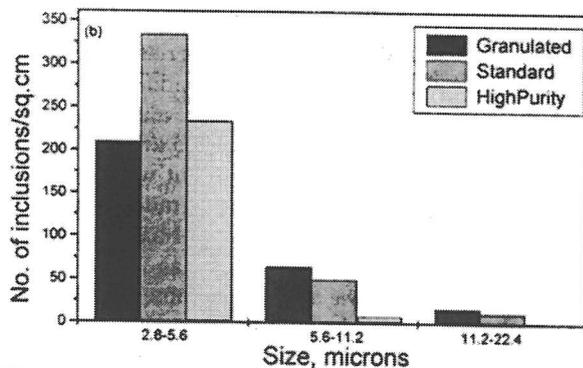


Figure 8. Average area-% of inclusions in tool steels²³.

It is obvious that more studies are needed to get a comprehensive picture of the inclusion characteristics in ferroalloys. It is important to provide information of total oxygen content and inclusion compositions as well as of micro and macro inclusion size distributions. In this way, the demands from the customers in the steel industry can be met.

3.3 In the Future

It is very likely that in the future very strict demands on inclusion characteristics in

ferroalloys will be required from the customers in the steel industry. It is possible that specifications on inclusion size distributions and compositions will be a demand, very similar to the specification of the alloy or carbon content in the ferroalloys supplied today.

In the future, it will also most likely be a demand for ferroalloys containing quite many inclusions, but of a well known specific composition, and of a lower price. The reason is that if steelmakers can control the inclusion characteristics during production better, they will learn how to handle ferroalloys containing more inclusions. Therefore, there is a cost advantage if they can buy cheaper less refined ferroalloy grades. In order to use these grades, the majority of the ferroalloy additions will have to be moved to earlier in the process. Instead of adding the ferroalloys at the ladle treatment station, more additions will take place during tapping from an electric arc furnace or a converter. In this way inclusions that are supplied from ferroalloys will have the chance to get separated to the top slag. Later, this top slag can be raked away, before a synthetic slag is added in the ladle treatment station.

The addition of cheaper ferroalloys earlier in the process is not a new development. It has happened before in the production of stainless steel. Stainless steelmakers used to buy a more refined and more expensive FeCr grade and add it in the AOD converter. Nowadays, they buy a cheaper and less refined FeCr grade and add it in the process step before the AOD, namely the electric arc furnace.

There is another additional development of ferroalloys that can be expected in the future. Namely, cleaner ferroalloy grades containing few inclusions and of a very specific composition. They can be more expensive than ferroalloys on the market today. The use of these will primarily be for late additions during ladle refining. One example is if the specification of an alloy content has not been met, more needs to be added. Since, this late in the process the steel is very clean with respect to inclusions, the extra addition should not be allowed to contaminate the steel more than

necessary. If a ferroalloy with a higher inclusion content is used, additional stirring is necessary in order to promote the separation of inclusions. This will result in lower productivity and higher production costs.

The new and more clean ferroalloys to be developed can also be used for grain refining of steel, which is discussed in another paper presented at the conference.²⁷

4. CONCLUDING REMARKS

The ferroalloy industry has supported research to increase the knowledge of inclusion characteristics for some ferroalloys. However, this needs to be done for all ferroalloys. The inclusion determination also need to be done on a regular basis. In principle, it needs to be done for each heat. In the near future the customers in the steel industry will expect to receive information regarding size and composition of inclusions as a complement to the analyses of the elements that are dissolved in the ferroalloys and that are provided today.

It is also possible that the customers in the steel industry will demand upper and lower specification limits on inclusion sizes of micro and macro inclusions as well as compositions.

The new possibilities in the steel industry to obtain more information of micro and macro inclusion characteristics can lead to two major scenarios. The first is that ferroalloys of lower cost and with a higher but fairly well known inclusion characteristics will be attractive. This is under the assumption that they can determine the inclusion composition after alloy addition and can compensate for the higher inclusion content by a process change. That process change can, for example, be to add the ferroalloys earlier in the process and prolong the stirring in order to promote collisions and removal of inclusions. Secondly, that a very clean grade of ferroalloy will be demanded with strict specifications of inclusion characteristics. This grade is to be used for late additions in the process when the alloy specification in the steel is not met. Furthermore, it is for use as grain refiners.

Finally, it should be pointed out that the ferroalloy industry still has the time to act to meet future expected demands from the customers in the steel industry. Only a few steel companies have access to the latest technology to obtain information on inclusion characteristics. If the ferroalloy industry work together with these steel companies, which use the cutting edge technology to gather information on inclusion characteristics, both parties will benefit. The majority of the steelmakers in the world will follow the ones leading the new development. Therefore, the ferroalloy industry can be prepared to meet their future demands when they ask for it.

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