Plenary Address: The Chemistry of Chromium Alloys for the New Stainless-steel Processes

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SYNOPSIS

The paper deals with the new processes for the production of stainless steel that have been used increasingly during the last few years, as well as with their influence on the consumption pattern of chromium alloys.
The VOD (Vacuum Oxygen Decarburization), AVR (Allegheny Vacuum Refining), AOD (Argon Oxygen Decarburization), and CLU (Creusot-Loire-Uddeholm) processes are dealt with separately, primarily in regard to the influence of carbon and silicon on the charging conditions and to the limits of the contents of these elements. Alternative procedures and the choice of chromium alloys are also discussed.

INTRODUCTION

At the time this paper was written, there was no real clearcut opinion on the optimum composition for the chromium alloys to be used in the new steelmaking processes. We expected, however, that today we would be in possession of further detailed information on this score. However, opinions still differ greatly and, consequently, the emphasis in this discourse is still on the processes themselves, rather than on the chemistry of the chromium alloys to be used.

As you all know, stainless steel was for many years manufactured almost exclusively in a single-step process in arc furnaces, the melt being decarburized by oxygen refining at atmospheric pressure. This process is, of course, still being used in many steel plants all over the world. Owing to the carbon—chromium equilibrium prevailing in a steel bath under these conditions, the decarburization has to be done at a low chromium content in the bath if the desired final carbon content is to be achieved. The remaining amount of chromium required to bring the chromium up to specification has to be added, after the decarburization, in the form of low-carbon ferrochromium.

Although new ideas and theories had evolved for some time, it was not until the end of the sixties that steelworks generally obtained production units in which it was no longer necessary for the decarburization to take place at a low chromium content in the steel bath. As a consequence, the steelworks could then substitute high-carbon ferrochromium for a considerable part of their consumption of low-carbon ferrochromium. In *high-carbon ferrochromium*, we include both the 4—6 type and charge chromium.

These new production units were based on the principle that the decarburization should take place at a reduced partial pressure of carbon monoxide because the carbon—chromium equilibrium in a steel bath is very dependent on the partial pressure of the carbon monoxide in the gas bubbles created during the decarburization. This can be seen from Figure 1, which shows the carbon—chromium equilibrium in a steel bath at two different pressures of carbon monoxide and at two temperatures.

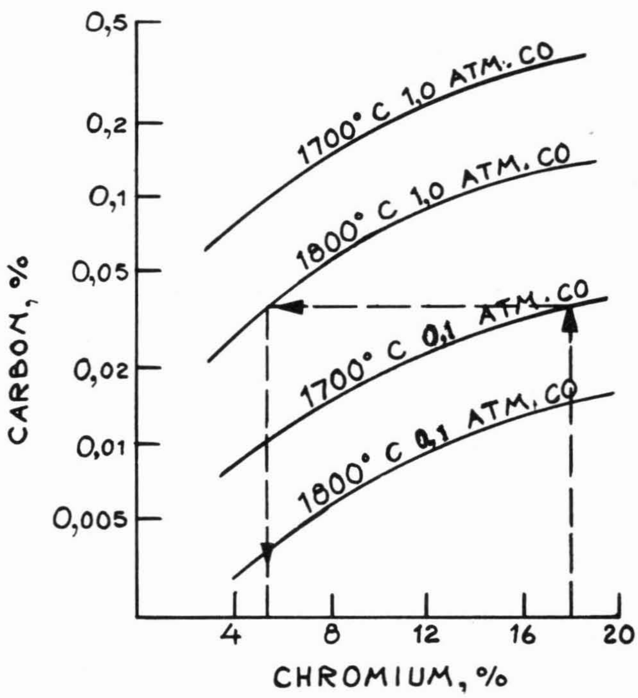

Figure 1

Carbon—chromium equilibrium at two different temperatures and pressures

For example, at a chromium content in a steel bath of 18 per cent, at 1700°C temperature, and at a carbon monoxide partial pressure of 0,1 atm in the gas bubbles formed during decarburization, a carbon content of 0,040 per cent can be reached. If, on the other hand, one has a carbon monoxide pressure of 1,0 atm in the gas bubbles, which occurs during refining in an arc furnace, one can allow a chromium content in the bath of only 5 per cent to achieve the same final carbon content, even if the temperature is increased to 1800°C.

The desired low partial pressures of carbon monoxide in the new stainless-steel processes have generally been reached in the following two ways:

(1) decarburization under vacuum, as in the VOD (Vacuum Oxygen Decarburization) and AVR (Allegheny

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Vacuum Refining) processes,

(2) dilution of the carbon monoxide with an inert gas, a principle that is practised today in the AOD (Argon Oxygen Decarburization) and the CLU (Creusot-Loire-Uddeholm) processes.

Through these new steel techniques, which are also being introduced into the production of ferro-alloys, the pattern of demand for chromium alloys has changed significantly. This can be illustrated by the development of the consumption pattern in the U.S.A. during the last four years. During that period, a rapid change has taken place from the conventional production of stainless steel in an arc furnace to production in AOD vessels (Figure 2). The number of AOD installations increased from one unit at the beginning of 1970 to 10 units in 1972 and 12 units at the beginning of 1973. It is considered that, during 1972, 40 to 50 per cent of the U.S. production of stainless steel was made in AOD vessels.

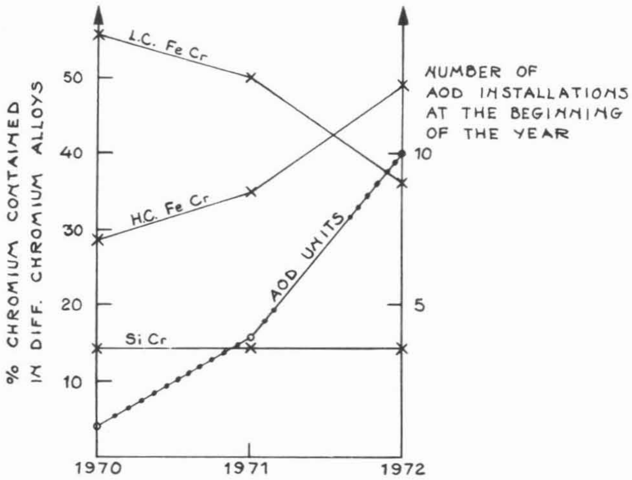

Figure 2

Consumption of different chromium alloys in the U. S.A., and number of AOD installations made during 1971—1972

The effect on the consumption of different chromium alloys can also be seen from Figure 2. As you can see from the consumption of chromium by chromium alloys in 1970, chromium in high-carbon ferrochromium contributed only about half of the chromium units added as low-carbon ferrochromium. This refers to stainless steel only, as do all the values in this diagram. In 1972, low-carbon ferrochromium decreased from about 57 per cent to something like 35 per cent, whereas high-carbon ferrochromium rose from about 29 to 49 per cent. In 1973 the difference was accentuated further, although the relations appear to have stabilized around a figure of 1,5 times as much chromium from high-carbon ferrochromium as from low-carbon ferrochromium.

If we accept the trends of this pattern, and believe in an entire switch-over to the AOD production of stainless steel, this will mean that only about 10 per cent of the chromium content of chromium alloys will be obtained from low-carbon ferrochromium. This percentage can then be compared with the figure of about 70 per cent, which was for many years the consumption (e.g., in Sweden), i.e. 70 per cent of the chromium in chromium alloys for stainless steel came from low-carbon ferrochromium.

The new processes have already drastically changed the consumption pattern for chromium alloys, and, as this may continue, we as alloy producers obviously have to follow this development very carefully so that we shall be able to supply the new steel processes with the alloys that they require.

THE NEW STAINLESS-STEEL PROCESSES

Even if all the new stainless-steel processes are based on the principle of reduced partial pressure of carbon monoxide, their requirements for what can be called an optimum chromium alloy are not identical. We have therefore chosen to deal separately with the new stainless-steel processes that have become widespread, and to indicate the practical and metallurgical limitations that will influence the choice of chromium raw materials.

The VOD Process

We have chosen to start with the VOD process, because this was the first process based on the principle of decarburization with reduced partial pressure of carbon monoxide. The development work for this process was done by Edelstahlwerk Witten AG, and the first unit started production in Witten during 1966. Today there are 12 plants in the world that have the equipment for this process.

A sketch of a VOD unit is given in Figure 3. The steel is normally melted in an arc furnace before being transferred in the reaction ladle to the degassing unit. In the vacuum chamber, equipment is installed for flushing by argon in the bottom of the ladle to get good stirring of the steel bath. Oxygen is supplied through a vertical lance on top of the bath.

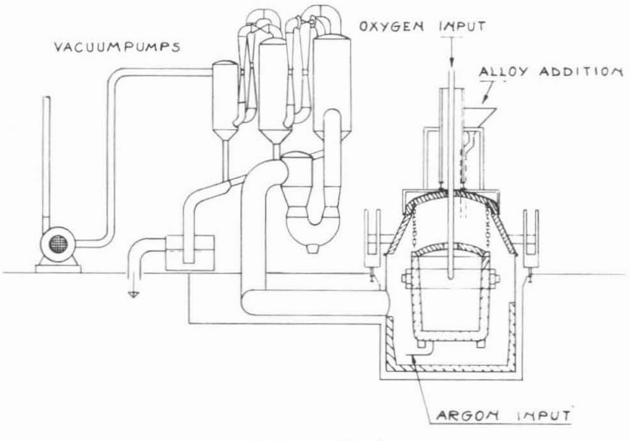

Figure 3

Explanatory sketch of a VOD unit

For practical reasons, there is a maximum length of time for which vacuum decarburization is practised. Normally, the carbon content is not permitted to exceed 0,5 per cent and the silicon content 0,3 per cent at the start of the vacuum decarburization, the main reason being that high carbon and silicon contents adversely affect the life of refractories as a result of the longer treatment time and the higher steel-bath temperature entailed. A high silicon content will give rise to an undesirable increase in the amount of slag generated during the decarburization.

There are two ways of obtaining the desired initial contents in the vacuum unit: by pre-refining outside the vacuum unit, or by selection of the raw materials so that the desired starting contents are not exceeded.

In the first alternative, the pre-refining is normally done in the arc furnace directly after melt-down, but it can also take place in an LD vessel, which is what happens at three

VOD plants. However, the choice of more expensive raw materials, thus avoiding pre-refining, could be justified, because it normally has many advantages, such as more production work and less reduction work in the interests of good chromium recovery.

The introduction of oxygen to a steel bath at atmospheric pressure will always result in a certain amount of chromium oxidation, but this is low at high carbon and silicon contents. This oxidation must either be accepted or be the object of reduction work, since, for obvious reasons, the slag cannot be transferred to the vacuum-refining vessel.

When pre-refining is adopted, high-carbon ferrochromium is the usual choice as carrier for the chromium.

Without pre-refining, the composition or chemistry of the chromium alloys to be used depends on the scrap situation, i.e. how much scrap and what quality of scrap one can lay one's hands on. If one is in a position to use a very substantial percentage of scrap, one can be less fussy about the composition of the chromium alloy to be used, whereas, with less scrap, a higher quality of chromium alloy will have to be used, even possibly a medium-carbon or low-carbon ferrochromium. Naturally, the carbon content of the other raw materials, such as ferronickel, is of great importance in the choice of chromium alloys.

The choice of chromium raw materials can thus differ, depending on metallurgical factors and scrap availability, and the use of a medium-carbon ferrochromium to eliminate the pre-refining step in the process should not be altogether disregarded as an interesting alternative.

THE AVR PROCESS

The first ASEA/SKF vacuum ladle furnace was installed in 1965. The equipment was intended primarily for the production of low-alloy steel, such as certain types of tool steel, but from 1969 it was also used for the manufacture of stainless steel. Today there are 25 ASEA/SKF installations in the world, of which 7 are adapted to stainless-steel production with pumping capacity and oxygen-blowing under vacuum.

The process is named the Allegheny Vacuum Refining process after Allegheny Ludlum, who have most experience in this process. Apart from the U.S.A., Belgium and Sweden in particular have used the AVR process.

The equipment, which is usually combined with an arc furnace, consists of a special ladle that is placed in a stirring coil standing on a transport wagon (Figure 4). The wagon with ladle and stirring coil can be transferred either to a heating station or to a degassing station. A description of the process was given at the 80th General Meeting of AISI on 25th May, 1972.

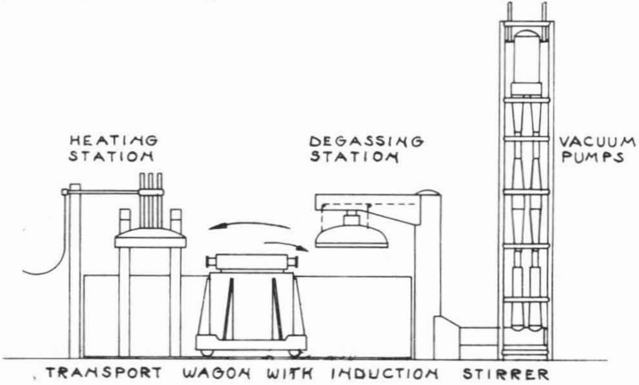

Figure 4
Explanatory sketch of an AVR unit

Owing mainly to the problems of lance life and splashing during vacuum refining – which have limited the possibilities for the use of low-cost chromium raw materials or have necessitated extensive pre-refining in an arc furnace – very small quantities of stainless steel are today being produced in the Swedish ASEA/SKF furnaces.

What has been said about the chromium raw materials in the VOD process also applies to the AVR process, but, owing to the heating possibility, the treatment times can be longer for the AVR process.

THE AOD PROCESS

In 1954, Mr V.A. Krivsky, Metal Research Laboratories of Union Carbide Corporation, found that simultaneous flushing with argon and oxygen acted as an excellent vacuum as far as the partial pressure of carbon monoxide was concerned during the refining of stainless steel. However, it was only 14 years later that this discovery was put to practical use on a production scale. To be exact, it was in April 1968 that Joslyn put their first AOD vessel into operation. During 1970, 4 additional vessels were started up, and since then there has been rapid development with new installations. By the end of 1973, there were 36 existing or planned installations in the world – a really fantastic development. A sketch of the side-blown AOD vessel is given in Figure 5.

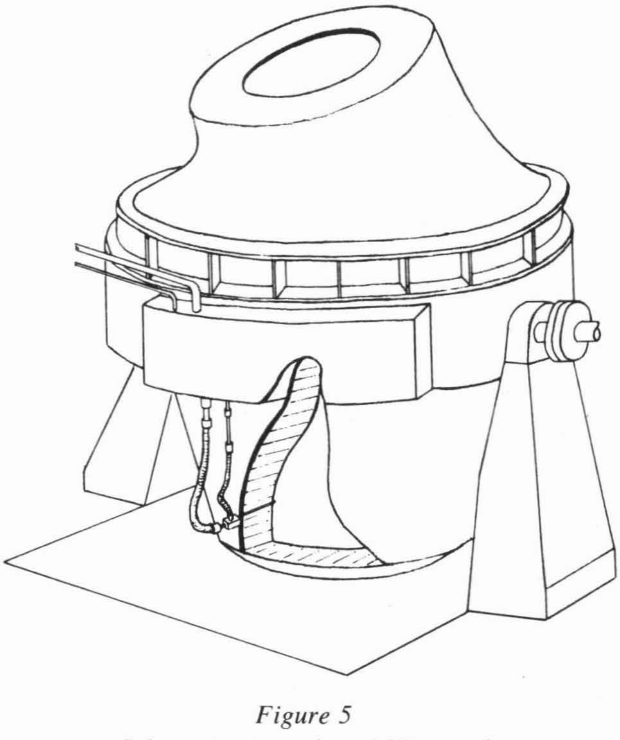

Figure 5
Schematic view of an AOD vessel

The expectations aroused by this process are due to its ability to decarburize steel of high carbon content, the simplicity of its equipment, and its good reproducibility.

There seems to be unanimous agreement that refining from high carbon contents does not involve any technical problems in the AOD vessel, but an increased carbon content means a longer treatment time in the vessel, which, in turn, has a detrimental effect on lining life. If, for example, the initial carbon content is increased from 0,5 to 1,5 per cent, the oxygen consumption increases to about 60 per cent and the blowing time increases accordingly. As the blowing time is considered to be an inverse measure of lining life, the increased initial carbon content means considerably shorter life. One way in which conversion costs can be minimized is to choose a somewhat more expensive ferrochromium alloy with a high chromium-to-carbon ratio, rather than to use the cheapest available chromium units.

It is generally felt that an initial silicon content of 0,4 per cent when the material is transferred to the vessel should be regarded as the maximum in the AOD process, and a reduction of the silicon content from this maximum value to 0,20 per cent is said to increase lining life considerably.

The required initial silicon content can be achieved either by the use of raw materials that will ensure the correct content, or by minimization of the silicon content through measures in the arc furnace that have already been discussed in connection with the VOD process, i.e. pre-refining with its possible disadvantages. It should be added that, from the point of view of chromium oxidation, a certain silicon content during melting-down in the arc furnace would, of course, be advantageous. Some state that the silicon content of the bath should be 0,8 per cent, and that it should then be reduced to less than 0,4 per cent. Others are of the opinion that a silicon content of 0,3 per cent is enough to limit the chromium oxidation during melting-down. Views on the optimum silicon content in the arc furnace depend to a great extent on how the slag reduction and deslagging are to be accomplished. If, for instance, one feels that local conditions allow time for slag reduction in the arc furnace, it may be in order to start with a higher silicon content, to blow, and to reduce; otherwise, one would probably have to accept chromium oxidation when reducing the silicon to a maximum of 0,4 per cent, or keep the silicon below that level from the start.

Ferrosilicon or silicochromium is used as the reducing agent after oxygen-blowing in the AOD vessel. The choice of reducing agent depends not only on the price of the silicon and chromium units, but also on the cooling requirements and the carbon content of the alloy. What is meant is that the chromium in a 40/40 silicochromium may sometimes be of advantage as a cooling agent compared with the use of ferrosilicon. It is interesting that, although these new steel processes require less silicon alloys than the traditional process, their consumption figures have so far not confirmed this, as can be seen from Figure 2.

When it comes to the chromium raw materials for this process, conditions are, if possible, even more complicated than for the vacuum processes. In the AOD process, it is essential to consider factors like the following, in addition to the conditions described above.

(1) Number of arc-furnace units to be run together with the vessel. One may have to start at low carbon and silicon contents in the vessel to keep pace with one's arc furnaces.
(2) Size of vessel. In a large vessel, the carbon and silicon contents have a greater influence on lining life.
(3) Number of vessel shells. If one has reserve capacity, one may tolerate shorter lining life as a result of higher carbon and silicon contents.

So far the question has been the choice between different types of high-carbon ferrochromium, where varying local conditions can result in quite different choices. In certain situations, however, a short operation time in the vessel may be of such importance that the use of medium-carbon ferrochromium is the best solution.

One of the advantages of the AOD process as compared with vacuum-refining processes is that it can cope much more easily with desulphurization. With a normal charge, there is usually at least 50 per cent desulphurization. If further removal of sulphur is necessary, a new slag is made of lime, fluorspar, and ferrosilicon or calcium silicide after the slag tapping, and after about 1 normal cubic metre of argon per tonne of steel has been blown in for stirring. In this way, very good sulphur purification is achieved. This procedure takes about 15 minutes. With large vessels, desulphurization is often used as an efficient means of cooling the bath before tapping.

Finally, the blowing of nitrogen as a flushing gas during the process seems to be an inexpensive and relatively easy way of including nitrogen in the product, i.e., it reduces the demand for nitrogen-containing low-carbon ferrochromium.

THE CLU PROCESS

Almost simultaneously Uddeholm AB in Sweden and the French steelworks Creusot-Loire were working on a technique for the refining of stainless steel with steam as a flushing agent. The steam dissociates in the steel, and the hydrogen acts as a flushing gas in the same way as argon in the AOD process, and the oxygen acts as a refining medium. In their process, Creusot-Loire also looked into the possibility of using tuyères with fuel-oil protection, which would permit the blowing of pure oxygen and the adoption of the modern technique for the refining of carbon steel. Thus, the refining could be done at high speed from very high initial carbon and silicon contents. In May 1973, Creusot-Loire and Uddeholm decided to present a joint converter process for stainless-steel production under the name of the CLU process, in which both steam and light oils can be used. A production unit of 70 tonnes, in which only steam is used, began operation in one of Uddeholm's plants in October 1973. Although operational experience is limited – about 15 000 tonnes of austenitic steel was made up to April 1974 – the process is mentioned here because it is likely to affect the pattern of chromium consumption. The design of Uddeholm's 70-tonne vessel is shown in Figure 6.

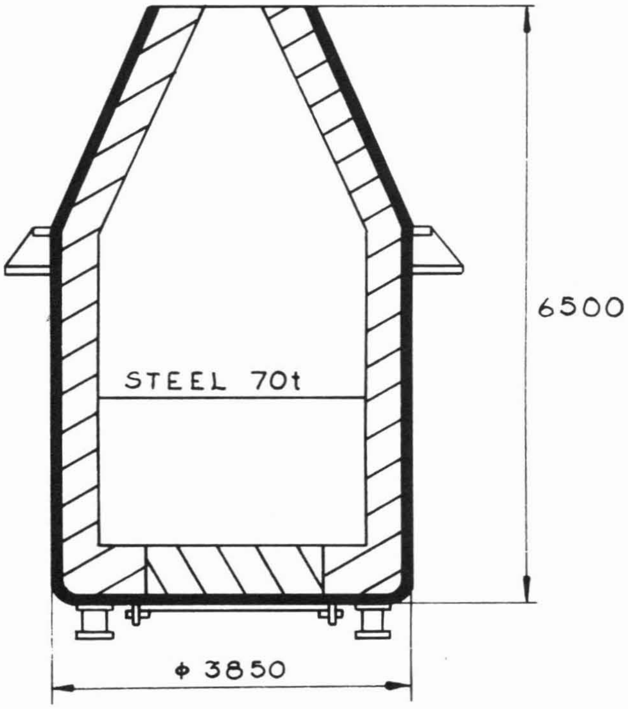

Figure 6
Cross-section of a CLU vessel

The greatest advantage of the process is said to be the lower operational temperature in the vessel (50 to 100°C) as compared with that in the AOD process. The extra chromium loss that this entails can obviously be counteracted by an extra addition of ferrosilicon for the slag reduction, which costs about 1,50 dollars per tonne.

The other major advantages of the method are reported to be

(a) the possibility of controlling the temperature during the decarburization (without the use of cooling additions) by variation of the relation between oxygen and steam, and

(b) the low cost of dilution gas, which is significant in the making of ELI steel.

From the point of view of raw material, there is a strong possibility that low-cost ferrochromium of high silicon and carbon contents can be used in this process. The low operating temperature and the fact that the vessel is bottom-blowing are expected to give very low refractory costs. Consequently, the prolonged treatment time at increased melt-in carbon and silicon contents would not necessarily mean substantially increased refractory costs in real figures. The typical composition of the melts so far decarburized is carbon about 2 per cent and silicon about 0,8 per cent, which permits the considerable use of charge chromium. The desulphurizing conditions are about the same as in the AOD process. It is pointed out that, from the point of view of desulphurization, a high silicon content is an advantage in arc-furnace operation. However, the higher melt-in silicon content must be compensated for by additional lime to maintain the slag basicity at an optimum.

To eliminate the hydrogen that is dissolved in the metal at the end of the refining period, about 1,5 m^3 of argon per tonne of steel is injected.

CONCLUSIONS

One very important factor in the choice of chromium raw materials has been referred to only superficially in this discourse, namely, the availability of stainless-steel scrap. During the past few years, most steel plants have been forced to work on a reduced proportion of scrap. This has resulted in a much greater interest in the composition of the chromium alloys to be used. The availability of scrap will naturally always influence the demand for chromium alloys and the required composition of those alloys. This fact, as well as the particular characteristics of the various new methods of stainless-steel making, makes it – at least in our opinion – impossible, or at least very difficult, for the time being to give a simple answer to the question of what is the most suitable chromium alloy for these processes. Each has its special requirements and possibilities; in addition, the local conditions in each case, including the quality of the other raw materials available, must be considered before one can volunteer an answer to this question.

To cope with the evaluation of this complex proposition, many steelworks have set up programmes for their stainless-steel production, which are then run through computers to show the optimum profitability of the steel production. One must therefore not entirely disregard the possibility of a certain nuance in the pattern of demand for chromium alloys that makes allowances for fairly modest variations in composition. Consequently, it is not altogether out of the question that we shall be faced with requests for made-to-measure alloys, which will require ferro-alloy producers to offer chromium alloys of varying chromium, carbon, and silicon contents. Steel plants will then be able to find a solution to the problem of chromium raw material. We doubt whether this prospect will create a tremendous amount of enthusiasm among ferro-alloy producers.