TUNDISH COVERING MATERIALS MANUFACTURING: REAL TECHNOLOGY IN TUNDISH METALLURGY

Riccardo Carli - Prosimet SpA, Via Rodi, 10 24040 Filago BG Italy
www.prosimet.com
Alessandra Del Moro - Prosimet SpA, Italy
Carlo Righi - Prosimet SpA, Italy
ABSTRACT

In the last decade steel making people has more and more achieved awareness of functions of tundish covering materials and their interactions with steel, so that one can state that not in depth approach to tundish metallurgy cannot be accepted.

At the same time tundish covering materials manufacturers have developed this consciousness: clear example of this contribution to maturation of this concern is given by Prosimet R&D Dept. experience on subject carried out during these years.

Different families of materials have been designed in order to fulfill different kinds of requirements. Present study deals in details with the description of technological characteristics of major two classes of materials: insulating powders and active powders.

KEYWORDS: tundish covering, insulating powders, active powders, double layer, NMI absorption, engineered products, holistic approach.

INTRODUCTION

In the last decades steel making people has more and more achieved awareness of functions of tundish covering materials and their interactions with steel.

Easily, one can state that in depth approach to tundish metallurgy is absolutely required for better steel quality achievement. At the same time, tundish covering materials manufacturers have developed same consciousness on this issue. This concern stems on the fact that tundish is not conceived as a simple distributor of steel from ladle to strands or a connection of a batch-type reactor to a continuous reactor, but as an actual metallurgical reaction vessel [1,2].

In the continuous casting process tundish is the last reactor with whom liquid steel comes in contact prior to solidification in the mould and in the secondary cooling sections. Taking into account residence times of covering powders in tundish, it’s easy to realize that tundish is the place where floatation of non-metallic inclusions, NMI, occurs and where steel maker has got the last chance to “clean” the steel, since among major functions of continuous casting powders NMI absorption capability has to be considered as a drawback affecting extensively its performance.

To investigate about floatation process great efforts have been done in modeling flow control in tundish: development of weirs, dams, turbostop® device are actual examples of realization of these researches [3]. Therefore tundish has a crucial role in the production of quality steels and this is the main reason that lead to a boosting research in tundish metallurgy and operations [4].

Near future will bring a new holistic approach to material developments: powders will be designed in connection with design of steel flow in tundish, development of lining materials, designing of ladle shroud properties with the aims of getting cleaner steel and longer casting sequences.

Different families of materials have been designed in order to take in consideration different kinds of parameters involved, essentially metallurgical targets or operative constrains. Among the first ones steel cleanness, steel chemical composition control, environmental issues and among the second ones casting time, sequence index, wearing of refractories.

Present study deals with the description of technological characteristics of major classes of materials. In order to give a more accurate description of technological characteristic of these materials we will describe them as insulating products or active products. These two classes will originate a third one which is the combination of the former ones: we will denominate it as hybrid configuration, commonly known as wafer or double layer system.

Survey will be conducted starting from the most insulating/less active material to the less insulating/more active material.

It will be clear that this classification criterion - insulating/active - is more modern and more effective compared to traditional acid/basic differentiation.
1 INSULATING PRODUCTS

1.1 HIGH SILICA PRODUCTS

1.1.1 RICE HUSK ASH BASED PRODUCTS

Rice husk is the film, exact term is tegument, that covers rice grains: it’s constituted by organic material, but it has got also siliceous component. It can be considered a bio-fuel since can be burnt in furnaces at 700°C – 900°C. Residuals of this process are ashes which essentially are composed by silica (ca.80% in weight) and un-burnt carbon (range about 5-10% in wt.) see “Fig.”1. Silica undergoes a phase transformation from amorphous to crystalline at temperature above 850°C. This material has been historically the first to be employed as tundish covering material. Its wide acceptance was due to easy availability all over the world, low cost, poor environmental requirements.

![Fig. 1: rice husk ash](image)

It’s a natural product and it is still the best from the point of view of insulating efficiency due to its low density in bulk (range 0.20 – 0.30 kg/dm³). In particular insulating layer of rice hull ashes according to this intrinsic physical characteristic is definitely perfect, being able to stand on very long sequences of casting without formation of crusts.

Then, rice husk ash provides excellent insulation, but on the other side even poor formation of slag in contact with liquid steel may cause a re-oxidation of steel due to high SiO₂ content of this covering material. Indeed, while nitrogen pick-up is mainly due to atmosphere contact -not perfect sealing of molten steel from ambient-[5], oxygen pick up is also directly caused by tundish slag. Actually, silica undergoes reduction especially with Al-killed grades and this exchange of oxygen between the slag and the liquid metal can result in a worsening of the steel cleanliness caused by formation of Al₂O₃ affecting also metallic silicon content.

Moreover, since carbon content of rice husk ash is minimum 3% in wt. with an average value of 5-10 % in wt. as stated above its use when casting ULC, IF steel grades is not so indicated, because of occurrence of recarburisation.
As discussed elsewhere [6] another phenomenon has to be considered: possible resulphurization of steel. Lime-based desulphurizing slag characterized by high sulphide capacity can pass from ladle to tundish during change of heat in the sequence: extent of this entrainment depends upon operative practice. Contact of ladle slag with high SiO\textsubscript{2} tundish slag reduces its sulphide capacity making the latter prone to release sulphur to the steel.

Another very critical aspect is related to working environment concern: thermal conversion of SiO\textsubscript{2} into crystalline cristobalite make it health hazard. This is one of the major driving forces in substituting rice husk ash based materials.

1.1.2 GRANULATED AND SPRAY-DRIED PRODUCTS

In order to try to limit environmental issues typical of rice husk ash based products spray-dried material having composition quite similar to rice husk have been developed. This material has been formulated using basically quartz or quartz sands. In spite of the fact that this material is produced with quartz, due to effective morphological control of grain size, breathable fraction of crystalline silica is very limited being under threshold limit values, TLV, established by European workplace health laws.

Same task has been reached by manufacturing through granulation process high silica nodules, having average size in the range 2-8 mm, see “Fig”.2

![“Fig.” 2: high silica nodules.](image)

1.2 HIGH MAGNESIA PRODUCTS

Designing of these materials has been a real breakthrough in the field of tundish covering materials. Idea was very simple: why don’t we try to cover the molten steel in tundish with a “particular lid” made of the similar material adopted to build the lining of the five faces of this parallelepiped-shaped box? Adopting an Italian gastronomy similitude one could say that to obtain an exquisite fish soup one should use an earthen pot with an earthen lid: covering the pot with a lid made of another material would lead not to get the same results as far as taste and cooking are concerned. Easy to think, but not to realize especially considering that we are dealing with granulated material.
Choice of correct raw materials, proper formulation, correct manufacturing of granules has been a real challenge: it has been necessary to proceed step by step in order to get most effective and efficient set up of technological parameters, see “Fig.”3.

“Fig.”3: MgO based spheroidal tundish powder

“Fig.”4: Phase diagram SiO$_2$-MgO-Al$_2$O$_3$ [7]
In the diagram phase $\text{SiO}_2$-$\text{MgO}$-$\text{Al}_2\text{O}_3$ these high-MgO powders having a MgO content in the range 75-90% in wt. are located as expected in the region of periclase showing melting point about 2000-2400 °C, see “Fig.”4.

Compared to rice husk ash based materials higher consumption is required to preserve same level of insulation: bulk density of these materials is in the range 0.70-0.90 kg/dm³.

However, if we have on one side less insulation, on the other side we have a big plus constituted by lower level of silica causing lower interaction with steel and refractories. Notwithstanding higher consumption, from the point of view of crust formation and duration of insulating layer in tundish this class of material gives satisfactory behavior.

In order to improve material performance, tundish covering manufacturers can add special carbon free in the range 1-3% in wt. to the original material in order to make it more effective on long sequences: then surface will be enough tender that operators can easily take samples of steel and can measure temperature. In this way an easy managing of operations in tundish is achieved.

Relevant difference compared with high silica powder is that silica content is very low, i.e. less than 6% in wt.: regarding re-oxidation of steel, this product presents almost no effects, see related discussion in paragraph 1.3.

Because of their higher price compared to traditional covering materials they are generally used in stainless steel casting production. Therefore also for this reason these materials are characterized by a limited C free content. Use for other steel grades having less strict requirements has also been observed in actual situations.

Slogan “do not touch the steel” summarizing the philosophy of use of MgO-based materials can be adopted in this case since there’s a little interaction between this kind of covering material and molten steel.

Regarding environmental workplace impact, this class of products is friendly since both chemical composition and physical aspect have low impact.

1.3 MEDIUM SILICA POWDERS

Next step taken after using rice husk ash has been the use of materials having a lower content of silica such as fly ash. They derive from coal combustion in power stations and due to this origin final carbon content of this material is in wide range (2-30% in weight generally).

This material shows peculiar property of being a mixture of glassy spherical particles containing silicon dioxide alumina and iron oxide and some crystalline phases. Basically it can be considered as a pre-fused or a pre-sintered material. Manufacturers of tundish powders can select among different types of fly ash in order to obtain desired free carbon content which has a leading role in establishing performance on long sequences.

Bulk density of spheroidal materials is in the range 0.70-0.90 kg/dm³ so to give satisfactory insulating behavior in tundish: similarly to MgO based materials consumption is higher in comparison to rice husk ash based materials. Crust formation on long sequences can be coped as above anticipated by regulating free carbon and by changing fluidity and solidification temperature of slag by the addition of elements like for example sodium, calcium and magnesium.

Products formulated with fly ash having a silica content in the range 30-40% in wt. have a totally different impact regarding reoxidation of steel compared with rice husk ash based materials whose content as previously reported is about 90% in wt.
It’s possible to clarify matter considering diagram depicted in “Fig.”5 which reports silica activity as a function of silica content, %wt., in CaO-Al₂O₃-SiO₂ ternary system [6]. As one can infer lowering in SiO₂ activity is caused by decreasing silica content in the product. Indeed, it’s pointed out that below 40% in silica weight silica activity decreased by one order of magnitude. From this point descent results to be very steep.

Based on their chemical compositions it’s possible to define two main classes of materials undergoing this classification of medium silica powders, mullitic phase based products and α - β-CS products (C stands for CaO, S stands for SiO₂).

Diagram in “Fig.”6 shows composition of mullitic phase based product in ternary system CaO-MgO-SiO₂ (with fixed content of alumina at 30%) approximating content in Na₂O. As one can notice from diagram melting point is about 1500 °C.
Diagram in “Fig.”7 shows composition of α - β-CS based products in ternary system CaO-Na₂O-SiO₂ (with fixed content of alumina at 15%): melting point of products is approximately in the range 1250-1300°C.

It’s worth to remark that α-β-CS products are last generation products. Recent trials in steel plants has confirmed that this class of product, better than mullitic ones, can effectively replace rice husk ash even for long sequences casting: suitable source and amount of carbon keep formation of crusts under control.

Generally, both families of products are formulated with a carbon content that does not suggest their use for ULC steel grades casting.

These powders are manufactured in spheroidal form so that uniform distribution on the molten steel surface is obtained and also from point of view of environmental work place issues impact is limited.

2 ACTIVE POWDERS

It has been remarked above that increasing demand for better quality steel led to a great effort in developing materials able to assure high covering and insulating properties and low corrosion activity of MgO-based lining material in comparison with traditional materials. This effort resulted in designing and manufacturing high MgO-based and medium silica powders. These products show respectively increasing capability of NMI absorption, characteristic which has been directly correlated with steel inner cleanness [5].

Active powders have been fundamentally designed to maximize absorption of NMI: this target can be achieved by an engineered powder that melting down in contact with steel generates an active slag layer, meaning with that, a slag able to effectively absorb NMI by virtue of specific viscosity and appropriate surface tension. Definition of engineered wants to stress the fact that tundish material manufacturer has tried to correlate the vector representing chemical-physical characteristics (formulation, selection of particular raw materials) to the vector representing behavior in tundish (NMI absorption ability). This process has been successful only wasting some insulating properties. This kind of powders are based on dramatically different concepts then
classical necessity to fulfill requirements of mere good thermal insulation. Therefore requirements of good insulation can be only re-obtained in this case by means of an insulating lid or by using another layer of covering material as it will be described in paragraph 3. This point stresses substantial difference between these new powders and more traditional high SiO\(_2\)-based or high MgO-based ones. These one-task insulating materials cannot effectively produce such a liquid protecting slag able to maximize the effectiveness of inclusions absorption. Active powders realize this effect on the basis of their particular \textit{engineered} chemistry. Based on their specific chemistries it’s possible to define two major classes of products: CaO-based materials and calcium aluminate based materials.

\textbf{2.1 CaO BASED MATERIALS}

This kind of powders being formulated upon suitable balance between CaO and other key components, all raw materials readily available, are actually the only products to be considered engineered. Their specific characteristics lead to the formation of slag able to optimize mass transfer at slag-liquid steel interface with consequent effect of maximizing NMI absorption capability.

Moreover, peculiar positioning of these active powders in a ternary phase diagram CaO-Al\(_2\)O\(_3\)-SiO\(_2\), see “Fig.”8 (red point), allows avoiding of formation of high melting point phases during casting, due to Al\(_2\)O\(_3\) pick-up from steel or mixing up with ladle slag that can accidentally escape from ladle shroud slag control device. Therefore, using this class of material can bring following important achievements: prevention of resulphurization by slag carry over from the ladle \cite{6}; prevention of the re-oxidation of the steel melt; prevention of nitrogen and hydrogen pick-up in molten steel. In particular as far as re-oxidation phenomena are concerned content in SiO\(_2\) of ca. 20-25\% limits the SiO\(_2\) activity to safe values of ca.10\(^{-3}\), see “Fig.” 5.

\textit{Fig.”}8: system Al\(_2\)O\(_3\)-CaO-SiO\(_2\) \cite{7}

Carbon content in these materials is added separately in order to keep in consideration both peculiar steel grade requirements (i.e. ULC grades casting) and melting rate of the products as a final balance of their properties in connection with casting requirements.
Remarkable aspect of these engineered formulations is that they can also be available in spheroidal material to fulfill strict environmental requirements. Plant experience in using these active powders has given very good results in the last twenty years.

2.2 CALCIUM ALUMINATE BASED MATERIALS

These materials are well known to give metallurgical active slags able to prevent sulphur pick up to the steel. It is a material obtained by complete melting in high-capacity furnaces of bauxite and limestone. It’s clear that compared to CaO based materials availability is completely different, depending on a limited number of suppliers so giving also reason for higher price. Similarly to CaO-based materials the use of this material allows to protect steel from atmosphere action and to realize absorption of NMI. These products show tendency if used in single layer themselves to give problem of formation of crusts and pasty layers. Their composition is shown in the diagram in “Fig.” 8 (black point). As it will be described in next paragraph both classes of products are commonly used in double layer combination with an insulating product.

3 HYBRID CONFIGURATION

Technology of insulating SiO₂-based and MgO-based powders in connection with development of active powders results in peculiar solutions for both major tundish metallurgical issues: insulation and absorption of inclusions.

“Fig.”9: double layer, hybrid configuration

Trying to combine these two important properties which are maximized respectively in insulating and active powders many steel plants adopted a combination of these materials in two layers, here defined as hybrid configuration. In contact with molten steel active powder will form slag whose
properties have been described above, while a layer made of insulating material, rice husk ash, SiO₂-based or MgO-based powders, will be exposed to atmosphere, see “Fig.” 9.
Evident advantages of this solution are: sealing of liquid steel surface by formation of liquid slag, excellent NMI absorption, good thermal insulation. However, preparation of this double layer is not so easy, it requires good practice, especially in preparation and maintenance of layers during casting. In particular, from a chemical point of view, using hybrid configuration, in case of upper layer constituted by high silica material is equivalent to increasing SiO₂ in a system containing CaO-Al₂O₃. Therefore, this mixing leads to hard surface formation due to solid precipitation of Gehlenite phase [8], see blue point in “Fig.” 8. In this case CaO-based products don’t produce any shell of hard surface in tundish in a double layer system remaining in the liquid phase.
On the other hand, using of MgO based powders as upper layer has opposite effect: with CaO based products crusting due to precipitation of periclase is expected, while with calcium aluminate is not.

CONCLUSIONS

In modern steel making, better steel quality achievement is given by depth approach to tundish metallurgy. Tundish covering materials classified in this work as insulating or active have to be used balancing their properties in order to maximize effectiveness of functions connected with all metallurgical and operational issues.
Boosting insulation and absorption of inclusions have been possible by developing two highly specialized classes of materials, whose combined use, as in hybrid configuration is at present the best solution steel makers can find in a challenge for better steel quality.
Further improvements in years to come could be characterized by synergy arising from joint designing of powders, steel flow modeling, lining materials, ladle shroud, tundish geometry, what here has been defined as holistic approach to tundish technology.

REFERENCES

4) TUNDISH OPERATIONS, Continuous casting Volume 10, ISS 1997
5) L.ZHANG and B.G.THOMAS, ISIJ Vol. 43 (2003), No.3, pp.271-291