# PROPERTIES AND CONTROL OF FLUXES FOR INGOT CASTING AND CONTINUOUS CASTING

**R. Carli, A. Del Moro, C. Righi**

*Present chemical-physical characteristics of ingot and continuous casting powders can be critically evaluated pointing out history of invention of these materials.*
*In an original tone, pioneering nature of first developments of casting powders will be described, illustrating empirical know-how of casting powders technology, based on trial-and-error method.*
*It will be originally emphasized that technology of continuous casting powders derives directly from studies and developments followed for ingot casting setting-up.*
*Latest developments will be analysed in terms of the value innovation business model.*

*KEYWORDS: casting powders, breakthrough invention, ingot casting, continuous casting, value innovation*

## 1.0 INTRODUCTION: HISTORICAL PERSPECTIVE

During 20th century major historical and economic events have shaped production of steel across the world, see Fig. 1 [1].
Early post-WWII-period attends first important challenge in growing steel-making field which was mass production. Production of steel scored a 7-fold increase since 1940 during a period of time generally named "The 30 glorious years". Of course, this achievement mainly stems from relevant breakthroughs in technologies of steel making and casting, such as secondary metallurgy and continuous casting. However, attaining better quality, which was vital characteristic for more and more demanding market, has been possible owing to what can be easily considered a real breakthrough invention.
Since 1910 steel was cast in ingot shape with some technical hitches in terms of operations and final quality of semis, see Fig. 2.
Significant improvements were made only across 1960's with launch of a new class of products named casting powders, i.e., powders to be used in steel casting likely to carry out some unprecedented duties as protect steel from oxidation, provide thermal insulation to liquid steel surface, absorb non-metallic inclusions, give some kind of lubrication.

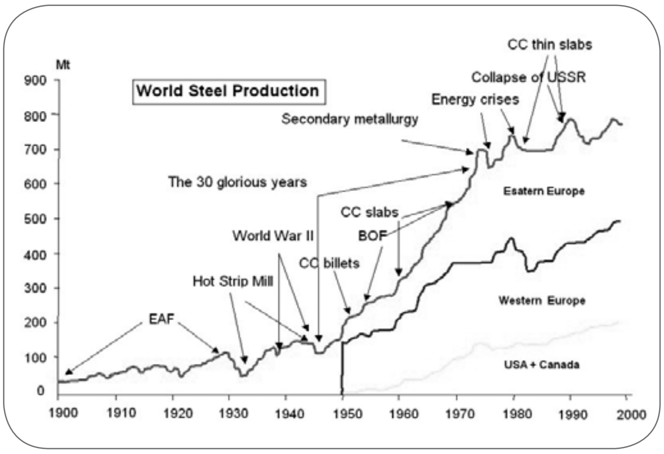


*Fig. 1* ***World steel production across the 20$^{th}$ century from Ref.[1].***
*Produzione mondiale di acciaio nel XX secolo da Ref. [1].*

## 2.0 PRINCES OF SERENDIP

"As their Highnesses travelled, they were always making discoveries, by accident and sagacity, of things which they were not in quest of". This was written by Horace Walpole in his letter to Horace Mann on January 28th , 1754 giving an example of such attitude of discovering things by chance and sincere observation of reality.
Although it's difficult to say that invention of casting powders was due to serendipity or empathy based on understanding of operations and fundamentals of steel ingot casting, it was surely triggered in 1957 by the encounter between Edgar Bolens, steel plant manager of Cockerill Seraing Steelworks, that time close to retirement, and young engineer Hans J. Eitel, working for Carl Spaeter Duisburg representative for Veitscher Magnesit, a well-known refractory company.
Bolens apprised Eitel about results of some experiments he

**R. Carli, A. Del Moro, C. Righi**
*Prosimet SpA, via Rodi 10, 24040 Filago BG, www.prosimet.com.*

Fig. 2
***"Ingot Molds", ca. 1910, rare Meissen porcelain plaque, Georg Haberecht (Germany), The Eckhart G. Grohmann Collection at Milwaukee School of Engineering.***
*"Ingot Molds", ca. 1910, raro dipinto su porcellana di Meissen, Georg Haberecht (Germania), The Eckhart G. Grohmann Collection alla Milwaukee School of Engineering.*

performed casting steel ingot with powders made by very poor components. This wide-open-minded young metallurgist, who served the German army as *frei williger* with Luftwaffe engineer corps in Travemünde, enthusiastically embraces that new idea, developing in 40 years many new products to modern commercial casting powders, [2-3].
With a sponsorship from Oerlichs GmbH & Co. KG, a company whose business was production of consumables for steelmaking, and commercial network of Carl Spaeter, Eitel started diffusing use of this new product, facing typical resistance to all new ideas of such dynamic but biased technical environment, [2].
He finally founded his own company Metallurgica GmbH & Co. KG in 1965. Three years later, Eitel hired from Bochumer Verein steel plant a young chemist, Heinz W. Schmidt, who'll came out to be one of most valuable of his co-workers.
Hans Eitel obtained a doctorate from Aachen University in his late 70ies, discussing a thesis on developing and manufacturing casting powders. This is still a significant document, not yet translated from German, reporting bright achievements of an entire life spent in following innovative vision of steel casting technologies [2].

## 3.0 POWDERS FOR INGOT CASTING

Early products were only mechanical mixture of few components, based on poor raw materials such as fly ashes, soda ash and milled coke. In spite of their simple compositions these materials featured a complete set of important properties, whose control was made through a proper balance of each component. While spreading on surface of liquid steel was assured by intrinsic characteristic of fly ash, addition of specific amount of soda ash allowed tuning of melting temperature, see Fig. 3. Moreover dosing of milled metallurgical coke prevented excessive consumption of powder during casting, controlling its melting rate.
Although these considerations appear almost trivial or evident even to dummy of casting powder field, it has to be considered those are actual observations, meaning with that, results of long and intense period of experimentations.
Dawning of casting powder technology was characterized by kind of magic, growing on that field of rough practice politely called trial-and-error method. Still basic know-how of casting powder technology is empirical one.
A significant flourishing of scientific knowledge has been recently recognized in this field, being analogically associated to scientific domain of formulation chemistry [4].

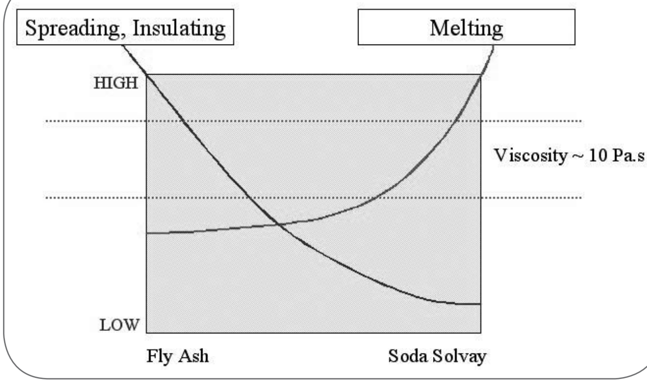


Fig. 3
***Pseudo-bi-dimensional phases space. Fly ash content and soda ash content were two parameters to be changed, modifying products characteristics.***
*Spazio delle fasi pseudo-bi-dimensionale. Il contenuto di ceneri e il contenuto di soda sono i due parametri che devono essere cambiati per modificare le caratteristiche dei prodotti.*

## 4.0 EXPLORING TECHNOLOGICAL PROPERTIES OF INGOT CASTING POWDERS

In the previous paragraph, past pioneering nature of development of casting powders has been evidenced. Initial random walking in a pseudo-bi-dimensional phases space - fly ash content and soda ash content were two parameters to be changed as depicted in Fig. 3 - allowed exploring technological properties of new products in connection with their physical and chemical characteristics. It was then possible to observe that different mineralogical and chemical compositions extensively affect spreading, insulation capability of powder layer, melting properties as melting temperature and melting rate, finally resulting in a better quality of cast ingot, see Fig. 4.
Relevant improvements of final steel ingot quality, as inner cleanness, better ingot surface and a profitable increase of process yield by reduction of pipe, were economic factors wid-

ening use of ingot casting powders.
It was also possible to understand that different ingot size and different steel grades may surprisingly require different products, i.e., products having different physical and chemical characteristics. Although main cause was relevant inconsistency of original raw materials in terms of melting rate or carbon content, it was clear from very beginning that some products tuning due to process peculiarities was required.

### Spreading and insulating

Concerning spreading, it has been already pointed out that this property of ingot casting powder derives from intrinsic characteristic of fly ash. In modern casting powders manufacturing technology, this characteristic is controlled by custom designed spreading test and eventually corrected with special additives. Good spreading of casting powder results in effective covering of liquid steel free surface, preventing re-oxidation due to steel contact with atmosphere. Moreover, homogeneous distribution of powder across liquid steel free surface combined with suitable thermal properties provides effective insulation to steel at ingot head even at the end of casting, contributing to pipe reduction. Thermal properties are generally correlated to apparent bulk density of products, in this case again correlated with intrinsic characteristics of fly ash. Similarly to spreading apparent bulk density, i.e., insulating properties is tested and eventually corrected with special additives in modern casting powder manufacturing technology.

### Melting

Controlling melting properties has been the first real job. Indeed, changing proportion between components, eventually adding some milled coke without knowing exactly related chemistry has required time intensive testing, brain storming and sometime luck.
Simple lab tests were set up to control these characteristics and to check deviations according to different chemistry. Actually, it was like to start playing around one of most important factor affecting melting of a flux which is lowest eutectic temperature which system can exhibit [6], see Fig. 5.
In spite of the fact that elucidation of mechanism of casting powders melting process is for some aspects still a research topic, changing of content of soda ash remains a rigorous thermodynamic approach.
Probably some failure analyses came out to be first insight on casting powder melting rate, evidencing that fly ashes with lower carbon content tended to melt faster. Trying to overcome this occurrence different milled coke was added with effect of obtaining kind of control of these characteristics.
Present knowledge of so-called coating effect of free carbon particles is based in a similar empirical approach supported by some mechanistic understanding [7].

## 5.0 CONTINUOUS CASTING: A NEW APPLICATION

The advent of new technology of continuous casting opened up a new application field for these new products. Actually, spreading of use of casting powders wasn't easy and immediate; success came only because of combination of a number of key factors.
Since early patents on continuous casting machine and their applications [8], major step forward of this technology was the commissioning of the world's first slab continuous casting plant in 1961 by Dillinger Hutte GTS, in Dillingen Germany. It's important to note that event was synchronic with initial spreading of use of ingot casting powder, see paragraph.2.
To prevent sticking of solidifying steel shell into the mold, lubricant drawn into mold/strand gap by mold oscillation has to be applied. Traditionally vegetable oils composed mainly by linoleic or oleic acid were used. Later mineral and synthetic oils were applied.
In spite of some drawbacks such as unstable distribution as well as Hydrogen and Carbon pick-up defects in steel, high breakouts and depression frequency, use of oil as lubricating agent was only choice [9]. Indeed, oil was used for many years in former Soviet Union countries even after introduction of modern powders for continuous casting.

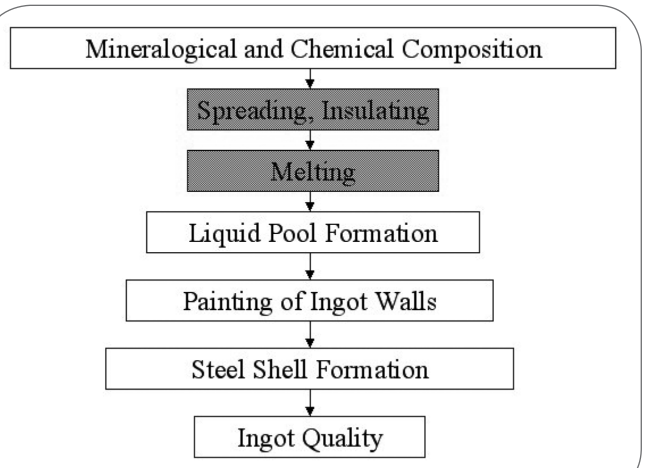


Fig. 4
***Schematic representation of mold powder performance stages, adapted from Ref.[5].***
*Rappresentazione a blocchi delle fasi di funzionamento di una polvere di colata, adattata da Ref. [5].*

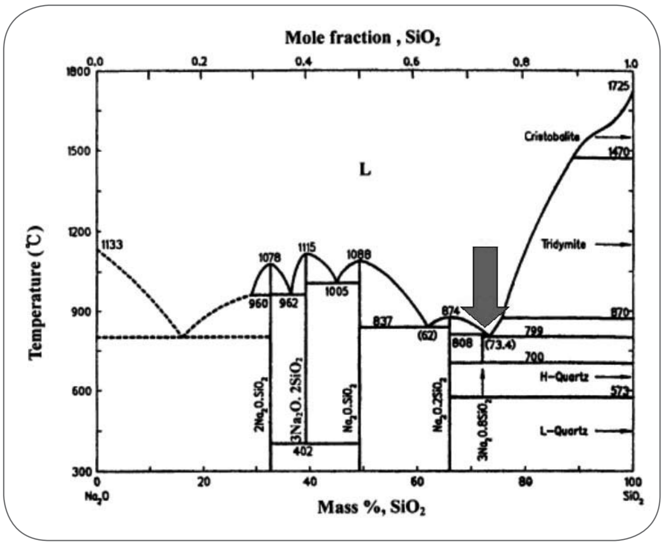


Fig. 5
***Equilibrium phase diagram of the $Na_2O$-$SiO_2$ binary system. Red arrow highlights lowest eutectic composition, from Ref.[6].***
*Diagramma di fase all'equilibrio del sistema binario $Na_2O$-$SiO_2$. La freccia rossa indica la composizione dell'eutettico più basso, da Ref. [6].*

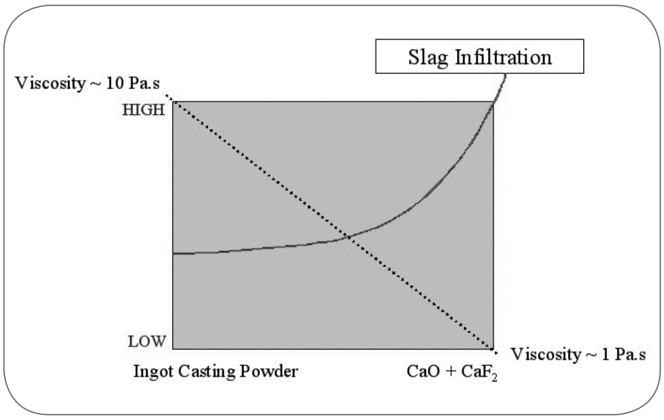


Fig. 6
***Pseudo-bi-dimensional phases space. Ingot casting powder content and CaO-CaF$_2$-based metallurgical slag content were two parameters to be changed, modifying products characteristics.***
*Spazio delle fasi pseudo-bi-dimensionale. Il contenuto di polvere per lingotti e il contenuto di slag metallurgico a base di CaO-CaF$_2$ sono i due parametri che devono essere cambiati per modificare le caratteristiche dei prodotti.*

Aiming to find better lubricating agent, first trial was made in Dillingen with a sample of standard ingot casting powder by steel plant technicians. Soon they realized that more sistematic and technical approach was required because of complexity of this problem. Therefore, supplier of this product was directly involved in this challanging development. Again, it's interesting to stress that encounter between those engineers and Eitel staff sparked research in this uncharted ocean.
From very first test was clear that infiltration of liquid slag resulting from powder melting was absolutely uneven and insufficient to assure good lubrication at least comparable to standard oil lubricant.
Starting from some ground knowledge of metallurgical slag chemistry, particularly related to slag fluidity, they tried to manipulate casting powder slag fluidity mixing original sample with different amounts of a metallurgical slag containing CaO and CaF$_2$. Thus, significant improvement of slag infiltration was observed, see Fig. 6.
Once more, it's worth noting empirical nature of approach followed to explore unfamiliar field of casting powders for continuous casting machines.
Remarkably, without exact consciuosness of mechanism affecting observed phenomena, these pioneers made significant stepforward to modern technology of continuous casting powder then properly named mold flux. From a chemical point of view mixing parent ingot casting powder with CaO-CaF$_2$-based metallurgical slag resulted in a shift from mullite to pseudo-wollastonite region in a ternary phase dyagram SiO$_2$-CaO-Al$_2$O$_3$. System was becoming more and more complex since chemical elements were playing a role, still not completly understood, in defining physical-chemical properties of molten slag. In particular, presence of Na, Ca and expecially F, was affecting number of tetrahedral coordinate cations, T, and non bridging oxygen, NBO, changing population of melt structural unit from Q0 to Q3, resulting in a relatively significant decrease of slag viscosity, see Fig. 7 [10].

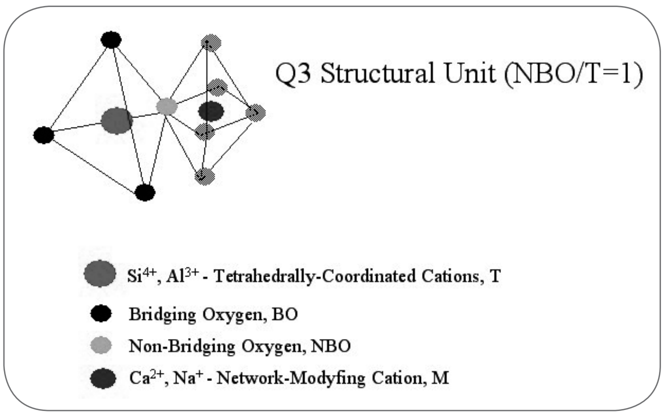


Fig. 7
***Typical structural unit of silicate glasses and melts.***
*Tipica unità strutturale di vetri e fusi silicatici.*

## 6.0 FROM INGOT TO CONTINUOUS CASTING MACHINES

In Fig. 8 similar scheme presented in paragraph.4 is reported. As one can infer, red coloured step represents technological properties being explored during challenging replacement of oil by casting powder, namely slag infiltration, while grey coloured steps represent attributes already investigated in development of casting powder for ingots. This consideration suggests that technology of continuous casting powders derives directly from early development of powders for ingot casting.
All characteristics discussed for ingot casting powders were actually borrowed by new products used in continuous casting machines and entire know-how was applied to develop innovative features of these new products. Of course bias cannot be excluded: modern casting powders actually have very peculiar characteristics mainly because of some historical reasons.

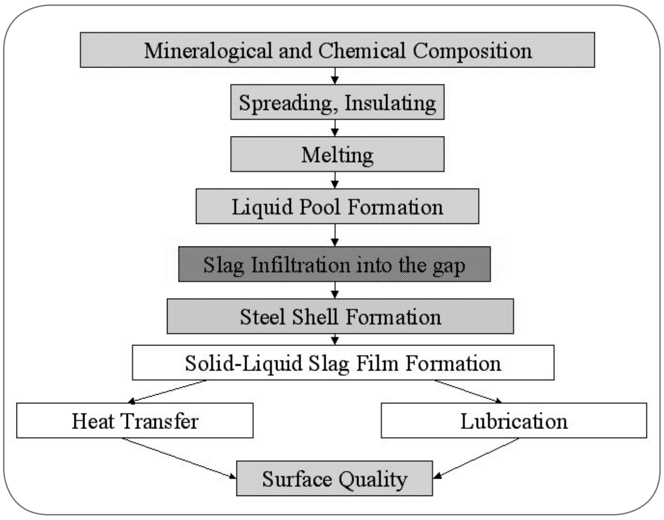


Fig. 8
***Schematic representation of mold powder performance stages, see Fig. 4.***
*Rappresentazione a blocchi delle fasi di funzionamento di una polvere di colata, vedi Fig. 4.*

All well-defined qualities built-up during ground-breaking studies on ingot casting powders play almost same role in new continuous casting products. However, powder melting and resultant liquid pool formation play far more important roles in continuous casting equipment, being these processes strongly related to availability of liquid slag for infiltration-lubrication.
Some tuning was required for further improvement. Then, random walking in pseudo-bi-dimensional phases space analogous to that one discussed in paragraph.4 - ingot casting powder content and $CaO$-$CaF_2$-based metallurgical slag content were two parameter to be changed as depicted in Fig. 6 - disclosed technological properties of new products.

### Slag infiltration

Infiltration of slag formed by melting of casting powder is most important technological characteristic of these products and most important factor controlling lubrication of strand forming in a continuous casting mold. As stated above, infiltration is enhanced by relative movement of mold and strand, particularly when mold is moving downward faster than strand.
As far as chemical features of casting powder are concerned, based on present knowledge it's clear that liquid slag viscosity and solidification temperature are major impact factors on infiltration-lubrication phenomena.
These factors are presently monitored by means of high temperature rotational viscosimetry, DSC (differential scanning calorimetry): important resources are continuously invested to improve effectiveness of these analytical techniques [7].

### Other properties

Among other steps in scheme depicted in Fig. 8, formation of solid-liquid film and heat transfer control are very recent topic of advanced casting powders expertise. Thus, lubrication only has been referred as most important breakthrough known from use of new continuous casting powders.
Since mold fluxes fundamental recognized functions are to assure lubrication required by tribological system of mold-solidifying strand shell and to provide crystalline phase solid film contributing to control heat extraction between strand and mold wall, researchers have been and are still making huge efforts in these areas of investigations.

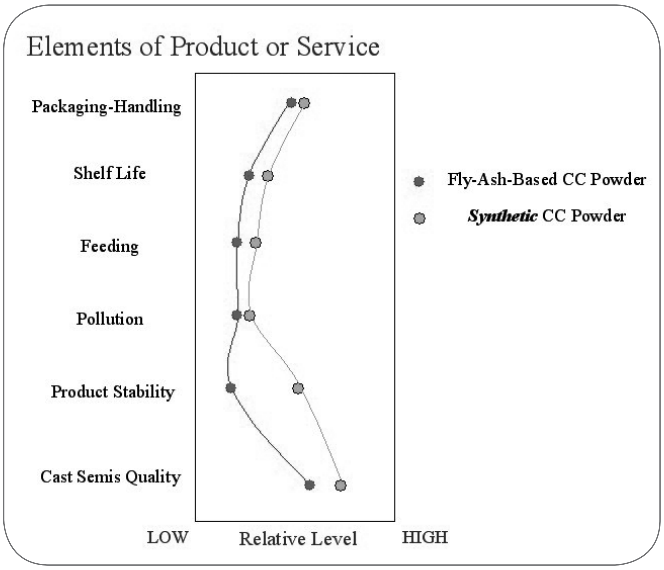


*Fig. 9*
***Value curve of casting powders.***
*Curva di valore delle polveri di colata.*

## 7.0 VALUE INNOVATION

Thanks to vertical growth of steel market along two decades, from 1960 until first big energy crisis, market of casting powders followed same trend up, showing an impressive expansion.
Reminding image given in paragraph.5 describing spreading application of these new products as a kind of ocean to be explored, it's possible to affirm that casting powders market has clearly been for many years a 'blue ocean', referring to business model discussed by W.Chan Kim and R.Mauborgne [11]. The statement is true mainly by virtue of ground-breaking nature of this innovation and fast market growth.
However, products were relatively weak with respect to reverse engineering and difficult to patent. Therefore, strategic focus for competing in such unlikely 'red-shifting' market was pursuing quantum leap in value, i.e., following so-called value innovation logic. In terms of product and service offering, value innovation consists in searching for the total solution customers seek beyond market traditional answers [11].
Major following achievements of casting powders technology can be explained as steps of specific value innovation process.

### Synthetic powder

Original fly-ash-based casting powders suffered some quality instabilities due to batch to batch variations of chemical analyses of fly ashes. Those were difficult to manage due to primitive analytical instrumentations. Solution was found using different raw materials with reasonably constant chemistry as milled quartz sand, Portland cement, calcium oxide, bauxite … etc., replicating known properties of parent product. Then, a new product family, denominated synthetic casting powders, was commercialised giving advantage of much more stable quality and performance.
Now, let's try to schematise value innovation logic behind launch of synthetic casting powders.
A value curve is drawn plotting performance elements vector of a product in a high-low scale allowing instant comparison with alternative products. These elements should describe aspects of product performance covering buyer experience cycle [12], likely to be very essential in case of a B2B goods. In the present work, some elements concerning casting powders have been considered crucial. Results are depicted in Fig. 9.
It's clear from value curve above proposed that synthetic casting powders were significant value innovated products for two elements where attention of end user was focused: better stability and improved quality of cast semis.

### Granulated powder

Similarly, it's possible to analyse another improvement step in technology of casting powder which was the control of morphological properties of products.
This relatively recent achievement resulted from application of well-known flash-drying process named spray-drying which consists in drying drops of sprayed water-based slurry by a

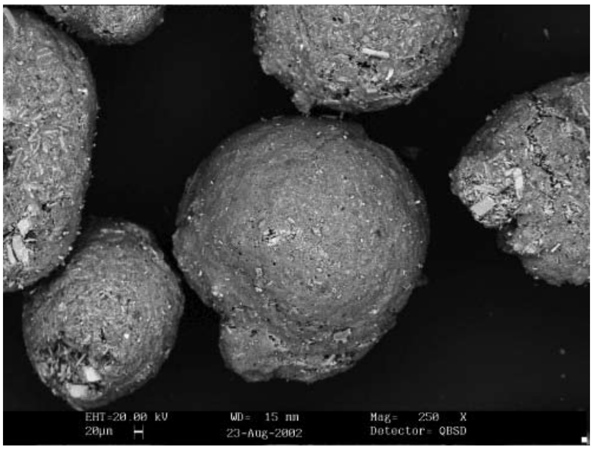


Fig. 10
**SEM pictures of a granulated casting powder.**
*Immagine SEM di una polvere di colata granulata.*

counter flow of hot air in a special designed drying tower. Typical spheroidal material obtained through this process is shown in Fig. 10.
This new product family was differently named from supplier to supplier as granulated, spheroidal, atomised casting powder.
The value curve of granulated casting powders is shown for comparison in Fig. 11.
It's evident that granulated casting powders were materials achieving significant value innovation of all product elements, from products shelf life to final quality of cast semis. In particular, control of pollution of working environment due to sharp decrease of fine residue and possibility to feed automatically continuous casting mold with dedicated special machines represented foremost characteristics to create a new 'blue ocean'.

## 8.0 CONCLUSIONS

History of invention of casting powders for ingot and continuous casting machines has been considered in order to give some elements for understanding present characteristics of these materials. Past pioneering nature of development of casting powders has been evidenced, showing that basic know-how of casting powder technology is empirical, i.e., based on trial-and-error method.
It has been shown that early achievements of technology of casting powders concern fundamental aspects of chemistry and physics of these materials. Then, it has been made clear that technology of continuous casting powder derives directly from development of powder for ingot casting.
More recent developments have been analysed in terms of the value innovation business model.

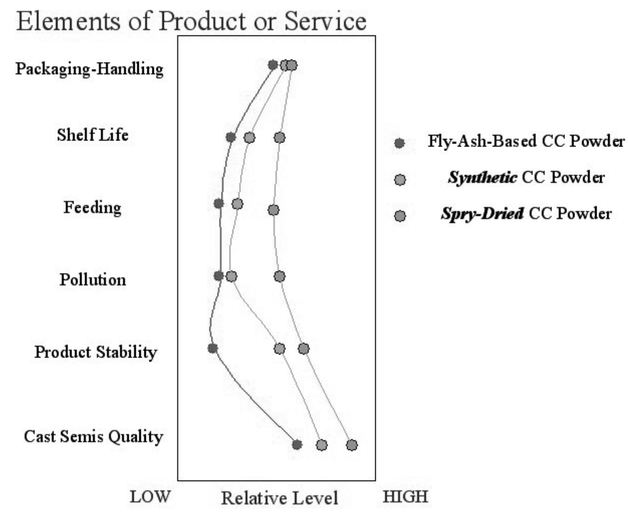


Fig. 11
**Value curve of casting powders.**
*Curva di valore delle polveri di colata.*

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# ABSTRACT


***PROPRIETÀ E CONTROLLO DI POLVERI DI COLATA PER LINGOTTI E PER COLATA CONTINUA***

*Parole chiave: acciaio, acciaieria, colata continua, storia metallurgia.*

*Le caratteristiche chimico-fisiche delle moderne polveri per lingotti e per colata continua possono essere valutate criticamente analizzando la storia dell'invenzione di questi prodotti.*
*Attraverso un approccio originale verrà descritta la natura pionieristica dei primi sviluppi delle polveri di colata illustrando il know-how empirico della tecnologia delle polveri basato sul metodo del trial-and-error.*
*Si spiegherà come la tecnologia delle polveri di colata continua derivi direttamente dagli studi e gli sviluppi seguiti per la messa a punto delle polveri per il colaggio dei lingotti.*
*Gli sviluppi più recenti saranno analizzati attraverso il business model della value innovation.*