Secondary metallurgy process optimization by alloying elements liquid addition

P. JIMBERT (1), M. ITURRONDOBEITIA (1), R. FERNANDEZ-MARTINEZ (1), J. I. BARBERO (2), M. SERNA (2), D. EGUIZABAL (2), A. ARTEAGA (3)

(1) Faculty of Engineering in Bilbao, University of the Basque country UPV/EHU, Paseo Rafael Moreno "Pitxitxi" 3, Bilbao, SPAIN
pello.jimbert@ehu.eus
(2) Tecnalia, Parque Científico y Tecnológico de Bizkaia, C/Geldo, Edif. 700, Derio, SPAIN
(3) Sidenor I+D, Barrio Ugarte s/n, Basauri, SPAIN

Abstract: - During the last years, numerous secondary metallurgical technologies have been developed. The present study presents a new technology based on adding all the alloying elements in liquid state. In this new process, a molten bath of the appropriate composition is made with alloying elements and deoxidants (in an induction furnace). This molten alloy is introduced into the liquid steel at the beginning of secondary metallurgy. With this new process, in addition to improving the mixing between alloy elements and steel, its final objective is to improve the process of secondary metallurgy in order to: reduce the time of secondary metallurgy, reduce the temperature of the steel liquid, use cheaper alloying elements, improve steel cleaning by reducing the addition of inclusions by ferroalloys, thus improving steel quality, increasing the efficiency of ferroalloys and increasing productivity. All this would result in lower energy consumption due to the reduction of electric furnace times and temperatures.

To achieve this goal, the first experiments with 100kg castings at laboratory scale have been performed, and the results are presented here below. Castings with solid and liquid addition of the alloying elements have been made and, the performance of the elements, the use of ferroalloys of different qualities and the final solidification microstructure have been analyzed, obtaining similar results in both processes. From these results we conclude that the viability and the necessary requirements for a future adaptation to the industrial environment of this new technology are feasible. Tests on an industrial scale are necessary for a real estimation of the savings and environmental improvements that would lead to the industrialization of this new technology.

Key-Words: - Secondary metallurgy, Liquid addition, Alloying elements

1 Introduction

World steel production has doubled in recent years, from 851 MT in 2001 to 1,656 MT in 2014 [1], most of it due to the growth of production in China. The percentage of steel produced with electric arc furnaces as the traditional fusion unit worldwide is around 45%, and this percentage is increasing. After the development of induction technology with high power units for furnaces of crucible with capacities over 65T, the induction furnace is offered as an alternative to the electric arc furnace for small steelworks [2]. In addition to saving the costs of the electrodes and the low requirements in the electrical network, the main benefits offered by induction furnaces are high performance from raw materials and low pollution of the environment and workplaces, since that induction is a method of heating without contact or flame.

Steel production processes are characterized by a high recycling rate of steel scrap. This is between 85 and 90% in industry and automotive, and 50% in the private sector [3]. Today the proportion of scrap used as raw material for steel production is between 40 and 45% of the total, almost equal to the use of iron ore, being a growing trend. Regarding the continued growth of global steel production, it is expected that the steel scrap recycling rate will be maintained, at least, at today's values and that the importance of direct reduction iron will rise , so we will have to continue advancing in the production of "electric steel". The most interesting element here from the technical and economic point of view, is the use of the "electric furnace" as the fusion unit in the production of steel. In addition to existing electric arc furnaces, it seems likely that induction furnaces will also develop in this context [2, 4]. Furthermore, given that the steel industry is an important CO_2 source, and in order to meet the EU´s climate and energy targets for 2030, it is expected a growth in the long-term electric furnace production.

The liquid steel obtained in the electric arc furnace is not yet the final product. Secondary metallurgy, also known as tap ladle metallurgy, is the set of processes and operations that aim to transform the liquid iron of the electric furnace into a liquid with a suitable composition and temperature to move to the stage of solidification. Its application results in a steel that meets the specifications required by the end customer.

During the last years, numerous secondary metallurgical technologies have been developed. In each of them, the most appropriate devices, reagents and instruments have been foreseen to achieve the aforementioned objectives. Various types of furnaces and other equipment are used for this purpose (ladles, converters, electric-heated tap ladle ovens and vacuum systems). Each of them has its specific role and is selected according to the particular necessities of the type of steel being manufactured. Examples are:

- Dust injection techniques (synthetic slag, alloying elements, rare earth metals, etc. acting through deoxidants and desulphurising agents are especially directed towards the modification of inclusions and the adjustment of sulfur and oxygen dissolved in iron liquid).
- Vacuum technologies specially designed for the degassing and decarburization of liquid iron (RH and DH processes and vacuum casting).
- Techniques for heating the metal in the ladle (tap ladle furnace) specialized in adjusting the composition, temperature and degree of oxidation of the liquid.
- Processes of addition of ferroalloys to the refined liquid from the BOF (Basic Oxygen Furnace) or the electric furnace, such as the CAS (Composition Adjustment System), which provide an optimum metallurgical performance during the addition of the alloying and deoxidizing elements.

In general, secondary metallurgy uses a variety of techniques: at atmospheric pressure, under vacuum, without heating, with heating, with agitation by inert gas or with the help of oxygen or reactive gases (special refining processes).

However, all these systems and techniques have in common that the addition of the alloying agents on the molten steel is carried out in solid state. This work focuses on the modification and consequent improvement of the steelmaking process by making total or partial additions of alloying elements and other conditioners in liquid state during the stage of secondary metallurgy.

The main added values that are expected with this new technology are focused on cost savings, through raw materials and energy and efficiency. It also improves the steel quality, flexibility and versatility of the facilities. This technology can be used both for common low carbon steels and for high quality steels.

Here are some of the advantages:

- Improvement of the performance of the alloying elements in comparison with conventional solid ferroalloys.
- Possibility of using ferroalloys of lower quality or smaller granulometry. Possibility of combining different types of ferroalloys with higher performance.
- As a coreless induction furnace is used to prepare the base alloy, it is possible to use controlled alloy scrap as a substitute element for ferroalloys.
- The performance improvement is not affected primarily by the amount of slag on the surface of the molten bath.
- As the process is faster, all the costs of the processes related to tap ladle metallurgy are improved (electric power, consumption of electrodes or the consumption of argon during agitation).
- The process is safer, because the addition of the alloy elements in a liquid state at a temperature of more than 1,300 °C minimizes fumes, dust in suspension and the risks of projection due to the absence of moisture. It also reduces the need for suction in secondary metallurgy with the consequent reduction in electricity consumption.
- The gas content of the steel is reduced due to the fact that molten alloy bath has lower gas content than solid ferroalloys and the addition process.
- Possibility of simplifying hopper systems or addition by wire. The addition by thread is much more accurate than the addition in bulk but also more complex and expensive. The liquid alloying agents may be complemented with it or even

replace it in some cases.
- Improvement in the addition process and the performance of specific elements such as Pb for steels with high sulfur, microalloy, refining, burrs or nanoparticles.

In summary, liquid addition allows a safer and more efficient alloy mixture with resource efficiency, as process times are reduced (energy efficiency) and cheaper raw materials can be used (cost savings) since the quality of ferroalloys is one of the factors that influence the final cleanliness of steel [5].

A better, more efficient use of ferroalloys would have a very positive impact on the reduction in raw material consumption and the energy efficiency of the process. In fact, since it is more efficient to dedicate the arc electric furnace to the melting and to do most of the metallurgical operations in the tap ladle, it is expected that the same type of improvement will be obtained, at least in concept, if a new installation is dedicated to the melting of ferroalloys. The possible benefit related to the reduction of thermal losses can be derived from Table 1:

Material added in steel (1 kg/ton)	**Change in steel temperature ∆T**
Coke	–65 **°C**
FeCr (50%), high-C	–41 **°C**
FeCr (70%), low-C	–28 **°C**
FeMn, high-C	–30 **°C**

Table 1: Effect of alloying additions on the change in temperature of the steel in the tap ladle for an average bath temperature of 1650°C. Addition to give 1% of alloying change in steel temperature element at 100% recovery [6].

Another idea about the possible benefits, can be found in Sampaio et al. [7]. In this work, in reference to a steel temperature of 1600 °C, the increase of 1 °C for each ton of steel would require approximately 0.2 kWh. Based on the samples collected during the period considered, an average steel reheating value of 7 ºC was found in 62% of the castings. The overheating value varied from 0.2 ºC to 65 ºC per casting. Considering a monthly production of 56,000 tons of steel and the average value of overheating found, an average reduction of 4ºC during this overheating would result in an annual saving of around US $ 125,000.00, which corresponds to 4.5% of the annual expenditure on electric power in the ladle furnace studied in the report.

In order to study the industrial viability of the liquid addition of the various ferroalloys, several 100 kg laboratory castings have been made. Different qualities of ferroalloys have been added in solid and liquid state and the following parameters have been analyzed: casting times and temperatures, technical feasibility of the new process, % of the performance of the different alloying elements in the final material and the solidification microstructure obtained.

2 Materials

The alloy selected for this study is 95Cr6. Its chemical composition appears in Table 2.

Element	**C**	**Mn**	**Si**	**Cr**
% of weight	0.95	0.3	0.2	1.5

Table 2: Chemical composition of the 95Cr6 alloy used in this work.

Two types of ferroalloys have been used to add the chromium to the 95Cr6 alloy. They are named FerroChrome Standard and FerroChrome Charge Chrome in the present work. The main difference on their composition is the chromium quantity. While the FerroChrome Standard has a content in chromium of up to 72% in weight, the FerroChrome Charge Chrome has around 5% less chromium and is considered a lower quality ferroalloy.

The reference casting with solid addition was carried out by melting 100 kg of the scrap selected for the project with the necessary ferroalloys to obtain the target chemical composition. All ferroalloys have been added in solid state. In the case of chromium, a ratio of 70/30 has been used in the distribution between FerroChrome Charge Chrome and Ferrochrome Standard respectively.

Another 9 castings of 95Cr6 grade have been made using the ferroalloys liquid addition methodology, with different recipes of liquid alloys and combinations of ferroalloys analyzed (see Table 3).

The methodology has been similar in all the castings, trying to be as representative as possible with respect to the industrial practice.

Name	FerroChrome Charge Chrome (%)	FerroChrome Standard (%)
K2	30	70
K3	50	50
K4	70	30
K5	30	70
K6	50	50
K7	70	30
K8	30	70
K9	50	50
K10	70	30

Table 3: Ratio of utilization of the different qualities of ferrochrome in the manufacture of the liquid addition alloys.

3 Results and Discussion

Casting with solid addition: With respect to chromium, the performance obtained (pending confirmation in longer series of castings) have been between 85 and 93% for the two ferrochromes used. The total duration of the casting was 1h2', with a maintenance period and composition adjustment of 19 minutes. Maximum working temperature was 1615 °C and pouring temperature in ladle of 1555 °C. The final composition can be seen in Table 4.

Name	**C**	**Si**	**Mn**	**Cr**
K1	0.94	0.23	0.30	1.7

Table 4: Final chemical composition in the ladle for the alloy process in solid state.

Casting with liquid addition: For castings using the liquid addition, different combinations of standard ferrochrome and ferrochrome charge chrome have been used. The temperature of the liquid addition is about 1460 °C at the time of pouring.

Experimental measurements of the liquid temperature of the mixture have been made by Differential Thermal Analysis techniques, obtaining values of experimental liquid temperatures between 1165 and 1230ºC.

Fig. 1: Images of the liquid temperature determination test using Differential Thermal Analysis techniques.

Fig. 2: Images of the process of liquid addition of the alloying elements to the base metal during the tests to evaluate the technical feasibility of the technology.

It is difficult, in individual castings, to perform an assessment of the performances associated with those elements with a high tendency to oxidation at temperatures above 1500 °C, such as manganese. In any case it should be noted that the chromium addition performance of the alloy has turned out to be greater than 98%.

After a slight adjustment, final castings compositions very similar to that of the K1 casting (Table 4) were obtained (see Table 5). Due to the small quantities of material used (in comparison with industrial processes) and the uncertainty of the process, there have been slight deviations from the specification (deviations that in no case invalidate or modify the analysis performed). In the same way, the modification of the process of melting and selection of raw material in order to achieve compositions more similar to the specification have generated a metal with percentages of gases that can sometimes be seen in the metallographic analysis. As we have mentioned previously, this fact does not alter in any way the analysis and study of technical feasibility carried out.

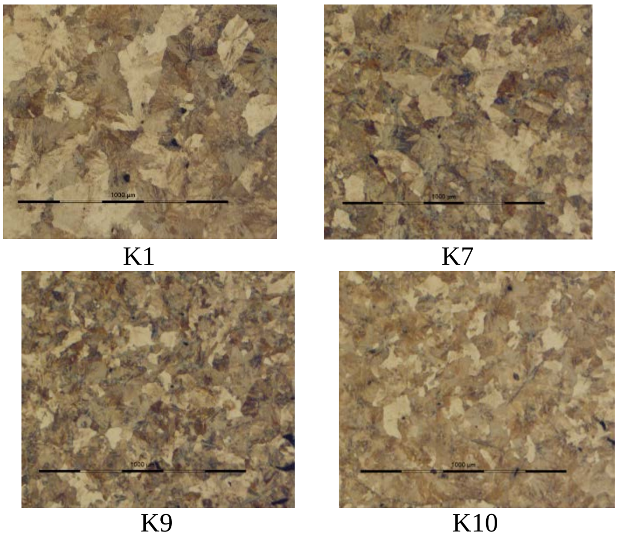
The total duration of the castings was between 1h5' and 1h12', with a maintenance period and adjustment of the average composition of 14 minutes (12'-16'). The maximum working temperature 1620 °C and the average pouring temperature of 1558 °C (1555-1565 °C).

Name	C	Si	Mn	Cr
K2	0.85	0.20	0.31	1.45
K3	0.86	0.21	0.28	1.48
K4	0.86	0.20	0.32	1.49
K5	0.95	0.31	0.41	1.60
K6	0.98	0.33	0.39	1.54
K7	0.96	0.28	0.40	1.55
K8	0.99	0.44	0.47	1.61
K9	0.98	0.42	0.48	1.59
K10	0.98	0.46	0.49	1.64

Table 5: Final composition of the nine castings made adding the alloying elements in liquid state.

It is convenient that all the results described here are confirmed by performing repetitive series of flows that minimize the uncertainty associated with the process and the analytical methods used.

The microstructures for all the alloys were observed with an optical microscope. The microstructures were obtained from the same area of the ingots for all the castings, in order to avoid possible differences due to the proximity to the walls of the mold or to the upper part thereof. The images were taken 20 millimeters from the bottom and 20 millimeters from the walls of the mold. The images obtained by optical microscopy of the different castings are shown in Fig. 3.



K1 K7

K9 K10

Fig. 3: Microstructures obtained for some alloys with solid addition (K1) and with liquid addition (K7, K9 and K10).

When analyzing the microstructures it can be observed that the K1 solid addition casting has a larger grain size than the rest of the castings presented in Fig. 3. In the absence of a more detailed study, the microstructures obtained point to a grain of smaller size in the castings made with liquid addition of alloying agents. Apart from these differences, both the porosity and the cleanliness obtained are similar in all cases.

4 Conclusions

- In the nine castings with liquid addition, it should be noted that the chromium addition performance of the alloy has been found to be higher than 98%, higher than the values of 85-93% obtained in the reference cast with solid addition.

- The use of lower quality ferroalloys in liquid addition has not influenced the achievement of the composition or the final desired microstructure.

- The final microstructure is similar in the samples obtained by solid and liquid addition in relation to its porosity as well as cleanliness.

- The grain size obtained in these very first experiments shows a smaller grain size for the alloys obtained with the liquid addition technology.

- The viability of the new process of adding ferroalloys in liquid state has been proved to be feasible, at the technical level (furnace temperatures and times, mixability, splash risks, ...) as well as in terms of the alloy obtained (final composition, microstructure, cleanliness, alloying elements performance, ...).

- An industrial-scale study is necessary to be able to make a real estimation of the savings obtained in the costs (use of lower quality ferroalloys, secondary metallurgy times) as well as in the environmental aspects (reduction of gas emissions and energy consumption).

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