USE OF ULTRA LOW CARBON CONTENT MAGNESIA-CARBON PRODUCTS FOR THE PRODUCTION OF LOW CARBON CONTENT SPECIAL AND STAINLESS STEELS

Hill, Keith[1], Gueguen, E[1], Silva, S.L.C[2], Brito, M.A.M[2]

1- Magnesita Refractories R&D, Europe, Itterpark 1, 40724 Hilden, Germany. Phone: +44-1909-552255 keith.hill@magnesita.com

2 - Magnesita Refractories R&D, Brazil; Av Cardeal Eugenio Pacelli, 815 – Contagem Phone: +55-31-33681486

ABSTRACT

The production of clean steels is becoming more common and this demands the use of special refractories in order to avoid contamination of the steel. Usually, for the lining of the ladles it is very common to use fired bricks as the carbon pick-up can jeopardize the steel quality. However, magnesia carbon bricks with very low carbon content can be an alternative to the fired brick. This paper shows the results of steelplant customer trials using this type of product in the production of low carbon special and stainless steels. The advantage of using this type of brick is a lower wear rate; lower cost and they don't show structural spalling at the same frequency as the fired bricks. A further advantage of the ULC brick is the lower thermal conductivity, which reduces the heat losses and the steel shell temperature.

INTRODUCTION

There is a continuous development of new high purity steel grades for specialist applications (eg Aerospace) with tight specifications for undesirable impurities and alloying additions. The development of secondary metallurgical routes has been a key driver in achieving these high purity steel grades and Table 1 (1) shows typical min/max values for important alloying elements in these steels together with the applicable secondary steelmaking routes.

Tab. 1 Content of alloying agents due to treatment in secondary metallurgy [1]

Element	Min./Max. Content [%]	Relevant Secondary Metallurgical Aggregates
C	0,0010–2,50	VOD/VD, RH, RH-OB, stirring station
Si	0,01–3,70	RH, LTS
Mn	0,08–20,00	LF
Cr	0,03–25,00	VD, RH, LF
Mo	0,01–4,50	LF or primary steelmaking
Ni	0,03–80,00	LF or primary steelmaking
Cu	0,03–3,50	LF or primary steelmaking
N	0,0020–0,5000	VD, RH, LF, stirring station
Al	0,0020–5,50	VD, RH, stirring station
W	0,020–6,50	LF or primary steelmaking
Co	0,03–10,00	LF or primary steelmaking
V	0,01–1,50	VD, RH, LF, stirring station
Ti	0,01–1,50	VD, RH, stirring station
B, Se, Te, Ca, Pb, S	0,001–0,300	stirring station, LF

Table 2 (2) shows the carbon content of various steel grades including ultra low carbon content steels which can have carbon contents as low as 10ppm for specialist applications.

Table 2 – Carbon content of various steel grades.

Type of Plain carbon steel	Carbon content (%)
Ultra low carbon (ULC)	<0.005
Extra low carbon (ELC)	<0.06
Very low carbon	<0.10
Low carbon	<0.25
Medium soft carbon	0.26 to 0.40
Medium high carbon	0.41 to 0.60
High carbon	>0.60

In order to achieve such low carbon levels in the steel it is important that that carbon pickup from the steelmaking process and the refractory lining is minimized. Some examples of areas where carbon pick-up can occur are:

- Graphite electrodes
- Alloying additives (eg Ferrochrome)
- Mould powders and tundish fluxes
- Oxidation of carbon bonded refractory lining during preheating process – although this can be minimized by the application of a glaze on the hot face prior to preheating
- Carbon pick-up from the lining after preheating.

In terms of the refractory lining then in order to achieve this target we see examples of the use of carbon free refractory products in the ladle lining for example fired doloma/magnesia enriched doloma products and fired magnesia-chrome products. Ceramically bonded products can suffer several disadvantages and examples are shown below;

- They suffer from slag infiltration and spalling of the products and as such you see increased wear rates.
- The maximum heat –up and cooling rates for the lining constrained in order to avoid thermal damage to the lining
- In the case of doloma products you have to take additional precautions during storage and use to avoid hydration.

The use of carbon-bonded products is one answer to minimizing wear by spalling and to allow faster heat–up and cooling down rates for the lining. Traditional magnesia-carbon products have 3-5% minimum carbon content and at lower carbon contents they do not possess the required thermo-mechanical characteristics for this application. This paper outlines the development and use of a new generation of ultra low carbon content (<2% fixed carbon) magnesia-carbon products, which do possess the necessary properties to achieve good service performance and in addition offer the following additional benefits compared with regular magnesia-carbon products:

- No carbon pick-up.
- Lower thermal conductivity which can translate into heat loss savings.
- Lower CO_2 emissions.
- Use of less natural resources during the manufacture of the product.

STEELPLANT EXPERIENCES WITH ULC CONTENT MAGNESIA-CARBON BRICKS IN SOUTH AMERICA

Product Concept.

The production of ULC content bricks is not as straight forward as reducing the solid carbon addition made to the bricks. Important factors to take into account when producing ULC content products (2) are:

- The use of an appropriate carbon source to maintain desired properties in particular thermal shock resistance in the final product.
- A binder system which imparts the necessary thermo-mechanical properties at very low total carbon content.
- Selection of appropriate brick granulometry/conformation pressure in order not to adversely affect thermo-mechanical behavior whilst ensuring a coked porosity low enough to give the required corrosion resistance.
- A production process which allows the manufacture of this type of product without carbon pick-up from previous batches of regular carbon content products.

Steel Plant Experience in SAM.

Using the product concept described before, industrial trials were conducted in the last 2 years, and currently we supply regularly this ULC brick for a steel plant making special steels and alloys including ULC steel which carbon content is below 15 ppm.

A resin-pitch bonded version of ULC brick (fixed carbon of 1.6 to 1.8%) has been used in the slag line of a ladle (25 ton) replacing fired MagChrome bricks. The main advantage of using such technology is a higher life which means higher equipment availability. When fired bricks are used for such application, due to the slag infiltration, the lining suffers a lot with structural spalling resulting in a very high wear rate. With the ULC brick no spalling is observed and the result is a more smooth wear of the lining and a more predictable lining life.

This steel plant has been using such product for more than a year with no spalling during the preheating step or during the operation. No carbon pick so far was identified in the final product (steel or alloy). Table 3 shows the comparison between the fired and ULC bricks.

Table 3 – Comparison between fired and ULC bricks.

	MagChrome Brick	ULC Brick
Brick Type	**Fired**	**Mag-C**
Average life of the Slag Line	10	17
Process Time (hours - average)	47	73
Wear rate (mm/heat)	10	5
Spalling Lining	Yes	No
Specific Consuption (Kg/ton)	8,4	5,5

EFFECT OF BINDER TYPE ON THE CHARACTERISTICS OF ULC CONTENT MAGNESIA CARBON PRODUCTS.

As previously mentioned in the paper then the type of binder will have a significant influence on the thermo-mechanical properties of ultra low carbon content products. Figure 1 (3) shows the effect of binder type on the relaxation behavior of 9%C magnesia-carbon products and you can see that the pitch bonded product does develop any significant stress up to 600 ºC because of the mesophase. Up to 600 °C we have a liquid phase present in the system that will work as a stress release mechanism. On the other side, for straight resin-bonded bricks this stress release mechanism is not observed. Once the brick is heated its expansion produces stress. In between there is the resin-pitch bonded brick showing an intermediate stress depending on the resin x pitch combination. Increasing the amount of pitch it is possible to reduce the stress level but not at the point of the original pitch bonded brick.

Based on the above relaxation behavior then it was thought that a pitch bonded version of the ULC content bricks could be a more interesting option. To investigate this in more depth we produced trial mixes of ultra low carbon content bricks in both resin –pitch and pitch binder and compare properties with a traditional 3% retained carbon pitch bonded product containing carbon black as solid carbon addition.

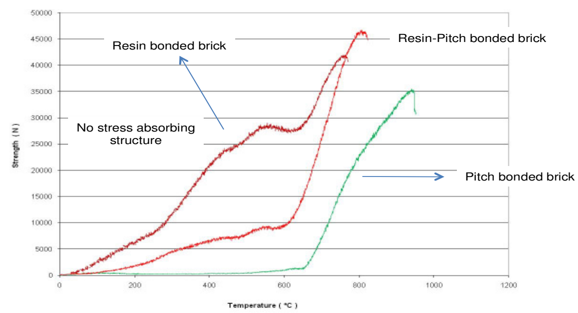

Figure 1 – Results of relaxation test after curing for different binders (heating rate = 5 °C/min).

A summary of the recipes used for the trial mixes are shown below, Table 4.

Table 4 – Recipes details for the trials.

Mix Code	Magnesia Quality	Solid carbon type and addition	Binder type	Other additives
RP1	97% MgO fused	0.8% special carbon source	2.3% Resin	0.5%
P1	97% MgO fused	0.8% special carbon source	2.5% Low BaP pitch	-
3% (reference)	97% MgO fused	1.7% carbon black	2.5% Low BaP pitch	-

All the mixes were produced using R&D pilot plant Eirich mixer in Hagen Germany and pressed into mini-key shapes using a hydraulic press. After pressing the bricks were heat treated on a standard tempering schedule in Hagen brick plant.

The main characterization results after tempering and coking are shown in Tables 5 and 6.

The results after tempering show that with the pitch binder system we achieve a higher density than with the resin binder. This may be related to the different viscosity and wetting behavior of the pitch at mixing temperature compared to the resin binder. The 3% carbon reference batch showed the highest density and this is probably related to the interactions between the pitch binder and carbon black addition.

In terms of cold compressive strength then the resin based product shows a much higher strength than the two pitch bonded products. The MoE values on tempered samples are all in a similar range. The HMoR value on the resin bonded version was higher than the pitch bonded ones.

After coking we see some significant changes in the characteristics of the products. The pitch bonded products show the highest density and lowest porosity values and this is probably related to the higher coking value of this binder system type. The coked cold compressive strength values of the resin and pitch bonded ultra low carbon content products are now at an identical level and similar to the tempered strength of the pitch bonded product. The 3%C reference pitch bonded product shows the highest density, lowest porosity and highest CCS value.

Table 5. Results after tempering

Property	RP1	P1	3% Reference
Bulk Density (g/cm3)	3.12	3.17	3.21
Apparent Porosity (%)	5.9	6.7	5.4
CCS (Mpa)	112	48	60
MoE (GPa)	61.4	59.5	72.4
HMoR(MPa)@ 1400 ºC -30mins	4.4	3.0	2.2

In terms of MoE value which will be an indicator of the expected thermal shock resistance of the product then the pitch bonded ULC product shows ~ 50% of the MoE value of the resin bonded ULC. The pitch bonded 3%C product shows a slightly higher coked MoE than the resin bonded ULC product and the fact that the pitch bonded product has ~ 3% lower coked porosity value has proved the overriding factor in this case.

The Retained carbon value of the products follows the expected pattern in that the resin bonded ULC shows a lower value than the pitch bonded one and this is related to the higher carbon yield from the pitch binder system. The reference product has the expected retained carbon value bearing in mind that it contains a higher weight % solid carbon addition compared to the ULC products.

Table 6. Results after coking at 1000 ºC

Property	RP1	P1	3% Reference
Bulk Density (g/cm3)	3.08	3.13	3.17
Apparent Porosity (%)	11.5	9.7	8.4
CCS (Mpa)	52	52	73
MoE coked at 1400°C(GPa)	17.0	8.2	19.4
Retained Carbon (%)	1.95	2.25	3.10

At such low carbon contents then the thermo-mechanical properties of this type of product is a very important characteristic. We measured the thermo-mechanical properties using the relaxation test after tempering and the HCS (hot compression strength) at 1400 ºC, both tests were carried out in a controlled atmosphere by the injection of Argon inside the furnace. The relaxation test was measured using a cylinder that was kept between a fixed bar inside the furnace. Under heating (5 ºC/min) is possible to measure the stress developed by the temperature. The HCS test is also measured using a cylinder coked at 1400 ºC and then under compression at the same temperature it is possible to measure the stress/strain curve.

Figure 2 shows the relaxation results for the 3 different qualities tested. The results show as expected that the pitch bonded ULC product shows better stress relief characteristics than the resin bonded version. The 3% C reference pitch bonded product shows slightly worse characteristics than the pitch bonded ULC product despite the higher carbon content. Maybe this is related to density or the type of solid carbon addition.

We know from steel plant experience in SAM that there are no problems with thermal shock issues with resin pitch based ULC product so the inference from these results is that the pitch bonded ULC should have better characteristics and it could be possible to reduce the solid carbon addition even further whilst still maintaining adequate TSR.

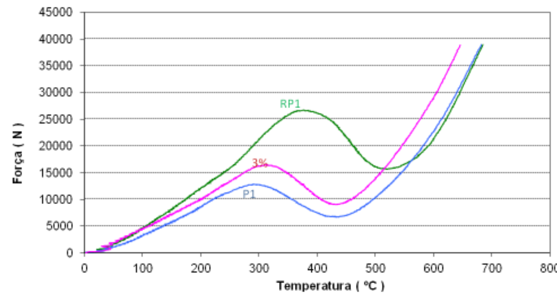

Figure 2 Results of relaxation test on tempered samples (heating rate 5 ºC/min)

Figure 3 shows the results of the HCS testing which shows that the pitch bonded ULC has a slightly lower maximum stress than the resin based one but shows higher deformation. The 3%C pitch bonded reference product shows the best characteristics with highest stress and highest deformation.

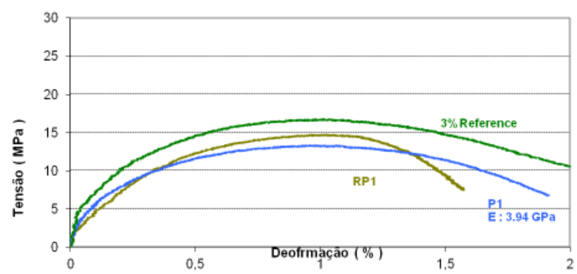

Figure 3 – Results of hot compressive strain test at 1400 ºC (heating rate 5 ºC/min)

In summary based on the properties we have measured then you can say the following:

- By changing from a resin based binder system to a pitch binder in a ULC formulation you have a product which has improved stress absorbing characteristics although the maximum stress achieved is lower than with resin bonded product. Therefore based on the load type (4) we have in the lining of ladles (strain controlled load) then you would suggest that the pitch bonded product would be a better option in this respect. So from the point of view of thermal shock resistance suggestion would be that the pitch bonded would be better suited. In view of the importance of thermal shock resistance then we will also test these samples using EN993-11 test method.

• Conversely the resin bonded system has higher strength values so from the point of view of abrasion resistance the resin bonded would be better suited.

• By virtue of a higher coking yield from the binder system then the porosity of the pitch bonded product after coking should be lower. In addition in this antioxidant free product then the pitch bonded version should have the better oxidation resistance. Therefore from the viewpoint of chemical resistance and oxidation resistance then the inference is that the pitch bonded version should show the better characteristics in this respect.

CONCLUSIONS

The combination of a special carbon source and an appropriate binder system it is possible to make bricks with <2% retained carbon with excellent thermal shock resistance and corrosion resistance for the production of special steels replacing ceramically bonded linings.

Experience in SAM steelplants producing special steels has shown that it is possible to successfully use this type of product and achieve a longer life and no carbon pickup.

The use of a pitch binder system in this type of product has shown some favorable results in terms of product properties and the indication is that this could lead to increased performance in certain applications although this needs to be verified with steel plant trials. In addition the improved stress relief properties of the pitch binder could allow the development of even lower retained carbon content products.

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