Use of Secondary Alumina-graphite as Raw Material of Alumina-graphite Silicon Carbide Refractories

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This paper discusses the possibilities to use spent alumina-graphite isostatic refractories (submerged nozzle, shroud, stopper) as a component of the raw material mix for the design of alumina-graphite silicon carbide used for torpedo ladles.

Different approaches were carried out to quantify the key parameters and to optimise the recycling process:

- sorting, cleaning and crushing of Al_2O_3-C continuous casting products
- investigation of secondary raw materials: size distribution, microstructure, chemistry composition and mineral phases
- design of alumina-silicon carbide-graphite bricks containing recycling alumina-graphite raw materials
- characterisation of the recipes and evaluation of their properties (chemistry composition; physical properties, mineralogy, microstructures)
- evaluation of oxidation resistance and corrosion resistance of the products.

The challenge is to develop new alumina-graphite silicon carbide refractories containing secondary alumina-graphite raw materials. The use of spent alumina graphite refractory material is restricted by the need to elaborate Al_2O_3-C-SiC high quality products that needs strict specifications. Consequently the amount of recycling raw materials was limited to 30 mass-%. In this case, the characteristics of alumina-graphite silicon carbide recycling refractories are similar to the usual qualities.

1 Introduction

Raw materials have a direct and immediate impact on the global cost structure of refractory products [1]. Their production is expensive and requires a lot of energy. Consequently, the use of recycled raw materials is an alternative challenge [2,7] to reduce the cost of refractories [8], to substitute the expansive raw materials, to secure access to the market, to reduce the energy requirement and to limit environmental impact (reduction of CO_2 green house gas due to the European Kyoto Protocole).

An evaluation of possibilities for the recycling of used refractories show the main sources of secondary materials are located in steel making. Indeed 65 % of refractories are used in steelmaking.

In particularly, the recycling of the alumina-graphite materials widely used in continuous casting process (monobloc stoppers, ladle shrouds and submerged nozzles) is particularly interesting.

These refractories are made with very noble raw materials: pure natural graphite flakes, brown corundum and zirconia-mullite aggregates. The combination of alumina with graphite gives these refractories excellent properties: thermal shock resistance, erosion, corrosion as well as high mechanical strength and low wettability by molten steel and slag. Natural graphite is classified by the European Union as a critical raw material because its economic importance [9].

Continuous casting pieces are independent of other refractories used in a steel plant; they are not mixed with other refractory materials; they are easily collected and should be easily recovered for recycling in a specific way.

After use, they are slightly worn and the contamination by steel, slag or mould powder is very limited. Therefore, this type of waste refractory can be easily recycled in new refractories requiring the simultaneous use of alumina and carbon.

This publication discusses the possibilities to use spent alumina graphite isostatic refractories as a component of the raw material mix for the design of innovative refractory products. Alumina-graphite silicon carbide bricks used in torpedo ladles are a suitable application. Indeed, torpedo ladles require the use of alumina-graphite silicon carbide refractories in areas specifically in contact with the slag. The quality is even better than that of bauxite based Al_2O_3-C-SiC bricks.

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Keywords: recycling, Al_2O_3-C secondary raw materials, Al_2O_3-C-SiC refractories, torpedo ladles

Received: 10.02.2013
Accepted:11.04.2013

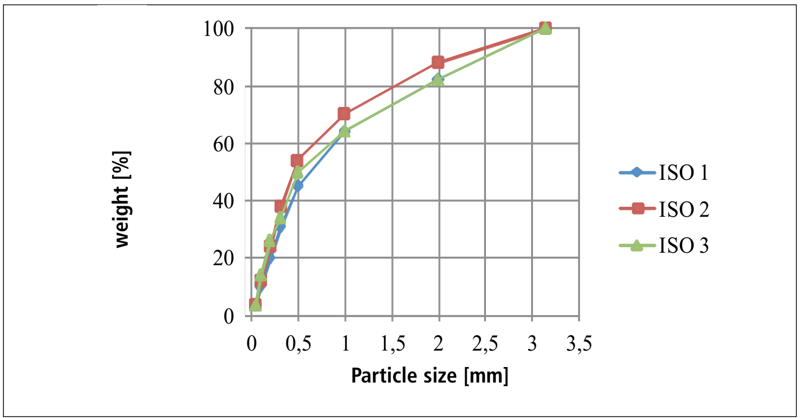

Fig. 1 Particle size distribution of Al_2O_3-C recycled raw materials (ISO 1: submerged nozzles, ISO 2: ladle shroud, ISO 3: stopper)

Tab. 1 Characteristics of Al_2O_3-C recycled raw materials

Aggregate	ISO 1	ISO 2	ISO 3
Piece origin	Submerged nozzles	Ladle shroud	Stoppers
Density	2,7	2,46	2,34
Chemical composition	[mass-%]	[mass-%]	[mass-%]
Al_2O_3	49,5	57,7	49,4
C	23,0	26,3	32,0
ZrO_2	16,0	0,87	1,87
SiO_2	6,2	7,7	13,1
Si metal	0,45	1,7	0,95
Fe_2O_3	1,05	1,54	0,38
CaO	0,73	0,2	0,18
MgO	0,38	1,34	0,98
TiO_2	0,77	1,0	0,79
Na_2O	0,73	0,62	0,61
K_2O	0,11	0,14	0,45
B_2O_3	0,93	0,82	0,93
L.o.I.	21,3	24,29	29,53

Different approaches were tested to quantify the key parameters and to optimise the recycling process:

- sorting, cleaning and crushing of Al_2O_3-C continuous casting products
- investigation of secondary raw materials: size distribution, microstructure, chemistry composition and mineral phases
- design of alumina-silicon carbide-graphite bricks containing recycling alumina-graphite raw materials
- characterisation of the recipes and evaluation of their properties (chemistry composition, physical properties, mineralogy, microstructures)
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The challenge is to develop new alumina-graphite silicon carbide refractories containing secondary alumina-graphite raw materials. The use of spent alumina-graphite refractory material is restricted by the need to elaborate Al_2O_3-C-SiC high quality products that need strict specifications. Consequently, for this application, it is not realistic to substitute the primary aggregates in a 1:1 ratio. The amount of recycling raw materials was limited to 30 mass-%.

2 Recycling procedure of alumina-graphite isostatic refractories (sorting, cleaning, crushing) and characterization of recycling raw materials

The objective was to evaluate separately the Al_2O_3-C recycled raw material of the different pieces of continuous casting.

The used refractories were collected and separated according the type of pieces (monoblock stoppers, ladle shrouds and submerged nozzles) and the altered zones and adherent metal or slag were removed from the surface of refractories.

So a specific procedure of recycling to collect and prepare each type of piece was defined.

- The treatment of the submerged nozzles was limited to break the lower part of the piece containing the frozen steel; the removal of the residual insulation alumina-silicate ceramic fibers (RCFs) was not necessary.
- The entire ladle shroud was recycled; adhering slag was removed.
- The stoppers were recovered from the slag heap using suitable mechanical handling equipments.

The Al_2O_3-C refractories were crushed and a magnetic treatment was carried out to separate and eliminate the portion of magnetic matter (steel particles, slag with iron oxides). At least, 60 mass-% of Al_2O_3-C refractory waste from continuous casting was recovered.

The particle size distribution of Al_2O_3-C secondary raw materials (Fig. 1) shows that the maximum size of aggregates is 3 mm. 50 % weight particles size are above 0,5 mm. There are quite a few fine particles.

The chemical analysis (Tab. 1) indicates that the secondary raw materials are not polluted; the major impurity is iron with a maximum of 1,6 % Fe_2O_3.

3 Design and characterization of the alumina-graphite SiC bricks

Three formulations of Al_2O_3-C-SiC bricks were prepared with 30 % Al_2O_3-C recycled raw material from stoppers, ladle shrouds and submerged nozzles (Tab. 2). Bricks were made at the laboratory scale by pressing at 150 MPa.

The main components, observed by microscopy, are two types of bauxite aggregates, the silicon carbide particles and the recycled raw materials. These recycled raw materials (in different forms: pellets of carbon, grains of corundum or mullite-zirconia, flakes of graphite and fine particles) differ depending on their origin.

For example, the ISO 1 brick, with recycled submerged nozzle inserts, contains grains of zirconia. The ISO 2 brick, with recycled ladle shrouds, is composed of corundum and graphite. The silicon additives are still present or converted to silicon carbide. Fig. 2 (a–c) show the microstructures of the Al_2O_3-

Tab. 2 Formulation of the alumina-graphite SiC bricks for torpedo ladles

Raw Material	[mass-%]
Bauxite	57
Recycled Al_2O_3-C aggregates	30
SiC	5
Other constituents	7
Binder	**[mass-%]**
Resin	5,5

Tab. 3 Characteristics of the alumina-graphite SiC bricks

Quality	Ref.	ISO 1	ISO 2	ISO 3
Origin of recycled raw material	–	Sub. nozzle	Ladle shroud	Stopper
Composition [mass-%]				
Al_2O_3	63,3	64,9	67,6	64,9
C	15,2	12,44	12,0	13,6
ZrO_2	0,08	4,02	0,33	0,61
SiO_2	10,3	7,85	10,6	9,28
SiC	8,1	5,76	4,5	6,2
TiO_2	2,0	2,13	2,16	2,17
Fe_2O_3	0,32	0,84	1,38	1,42
Na_2O	0,06	0,28	–	0,28
K_2O	0,17	0,2	0,2	0,32
B_2O_3	–	0,36	–	0,39
L.o.I.	14,3	11,9	11,7	12,9
Physical properties: Bulk density [g/cm³]				
As received	2,76	2,83	2,76	2,73
After 1000 °C coking	2,68	2,79	2,72	2,7
Open porosity [%]				
As received	6,73	7,6	8,58	9,11
After 1000 °C coking	15,2	15,21	15,35	15,23
Cold crushing strength [N/mm²]				
As received	151	90,6	90,2	86,1
After 1000 °C coking	66	68,2	66,8	66,7
PLC after 1000 °C coking [%]				
	0,5	0,12	–0,07	0,02

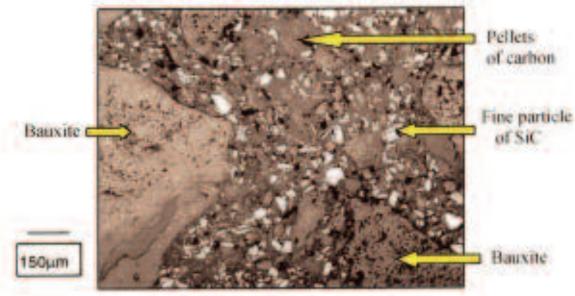

Fig. 2a Microstructure of the reference brick

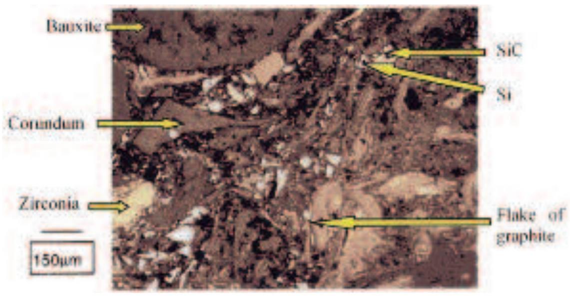

Fig. 2b Microstructure of the ISO 1 brick

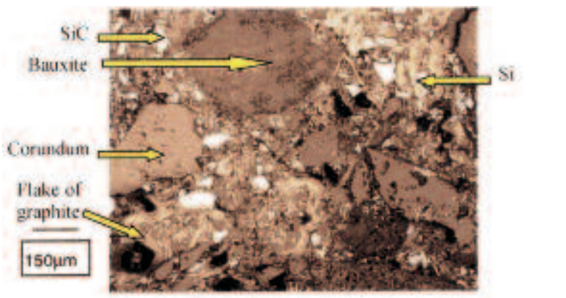

Fig. 2c Microstructure of the ISO 2 brick

Fig. 2 a–c Microstructure of the alumina-graphite SiC bricks

C-SiC reference and the ISO 1 and ISO 2 bricks.

The chemical composition and the physical properties, measured after coking at 1000 °C, are similar to those of the reference brick which does not contain recycled raw materials (Tab. 3). However, the ISO 1 bricks, made with recycled raw materials from submerged nozzle, have a slightly different composition due to larger amounts of ZrO_2.

In addition, after cooking, the recycled refractories are denser with a smaller pore size (Fig. 3) which tends to limit impregnation by iron and corrosion by slag.

The oxidation resistance was determined by thermogravimetry analysis (TGA). After cooking (at 1000 °C), the refractories were oxidized in air for 16 h at 1000 °C. The oxi-

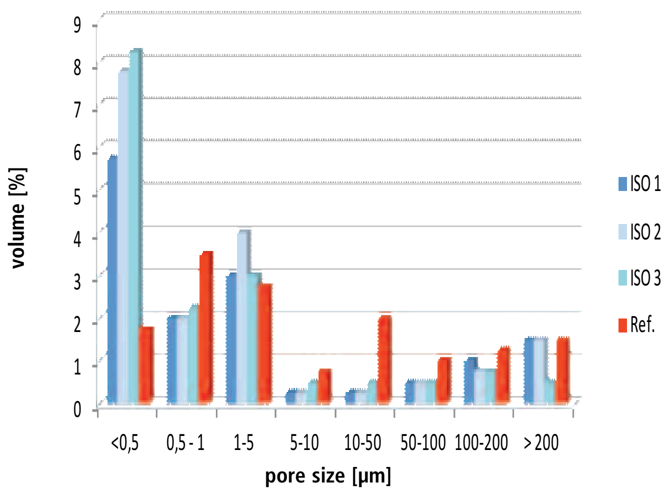

Fig. 3 Pore size distribution

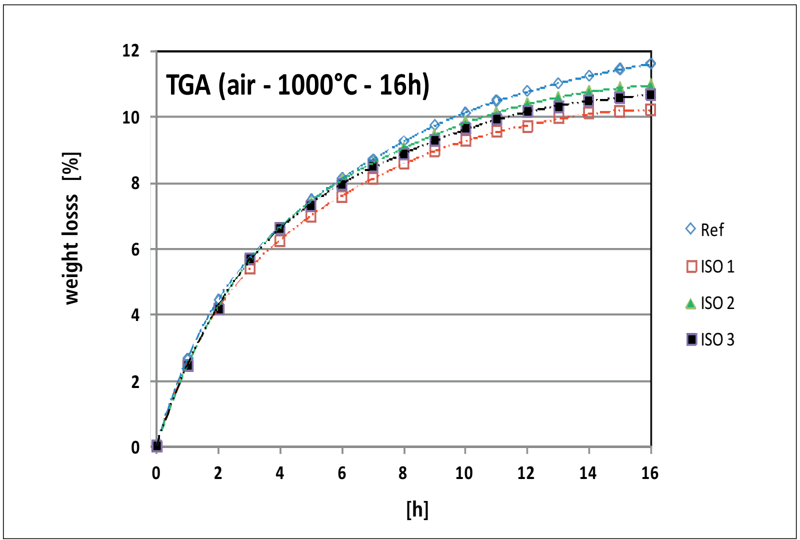

Fig. 4 Oxidation resistance of the tested alumina-graphite SiC bricks

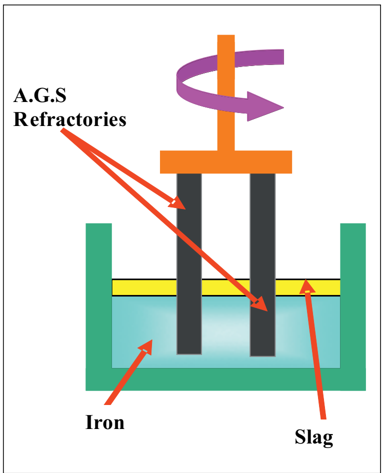

Fig. 5 Finger test

dation resistance of bricks containing recycled raw material is slightly better than the reference brick (Fig. 4). This interesting result is explained by the high quality of the graphite present in the raw materials recycled. This graphite is very pure and well crystallized. Also, it has a better oxidation resistance.

Corrosion trials by iron and torpedo ladle slag (with a CaO/SiO_2 basicity = 1,3) were performed at 1550 °C for 45 min using a dynamic (10 rpm) finger test (Fig. 5).

The corrosion resistance of the reference is slightly better than the ISO 1, ISO 2 and ISO 3 qualities (Tab. 4). These small differences are in relation to structural defects, due to manufacturing in lab. Industrial manufacturing must provide better mixing and better pressing.

4 Conclusion

This study covered the phases of recovery, preparation and analysis of materials for recycling and the assessment of alumina-graphite silicon carbide bricks for torpedo ladles.

Recycling of 30 % Al_2O_3-C raw materials is technically satisfactory with a lot of advantages: minimization of environmental impact, reduction of disposal costs, improvement of the quality of raw materials (corundum, zirconia). The characteristics of alumina graphite silicon carbide recycled refractories are similar to the usual qualities.

In this context, the secondary raw materials must guarantee the specific function of alumina-graphite silicon carbide refractories and the best practices should be applied to optimize the organization of recycling chains.

The next step will be to develop a formulation with a higher amount of recycled raw materials whose origin is:

- alumina-graphite materials used in continuous casting process (stoppers, ladle shrouds and submerged nozzles)
- alumina-graphite sliding gate plates [10].

The goal is to design high quality alumina-graphite silicon carbide bricks for torpedo ladles, containing corundum aggregates (indeed bauxites) with a 30 % reduction of the manufacturing cost.

Tab. 4 Corrosion resistance of the tested alumina-graphite SiC bricks (finger test)

Quality	Corroded Depth [%]	Corroded Volume [cm³]
Reference	24	4,71
ISO 1	25	5,02
ISO 2	25,9	5,32
ISO 3	30,5	6,98

References

[1] Maier, F.; Schmidt-Whitley, R.; Volckaert, A.: The contribution of refractories to the resource efficiently of industry. Proc. of Unified Int. Technical Conf. on Refractories (UNITECR 2011), CD, Kyoto, Japan, 30. Oct.–2. Nov. 2012

[2] Oxnard, R.T.: Why don't we don't recycle refractories in the USA. Proc. of Unified Int. Technical Conf. on Refractories (UNITECR 2005), CD, Orlando, FL, USA, 8.–11. Nov. 2005

[3] Crolius, R.W.: Environmental and safety and health regulations affectiong the U.S. refractories industry. Proc. of Unified Int. Technical Conf. on Refractories (UNITECR 2005), CD, Orlando, FL, USA, 8.–11. Nov. 2005

[4] Wittmer, D.E.; Petty jr., A.V.: Recycled materials for refractories. Ceram. Eng. Sci. Proc. **16** (1995) [1] 158–169

[5] Bennett, J.P.; Maginnis, M.A.: Recycling/disposal issues of refractories. Ceram. Eng. Sci. Proc. **16** (1995) [1] 127–141

[6] Noga, J.: Refractories recycling developments. Ceram. Eng. Sci. Proc. **15** (1994) [2] 73–77

[7] Hattanda, H.; Morimoto, S.: Refractory technologies conserving environment-future trend of refractory technologies suggested by current states. J. of the Technical Association of Refractories of Japan **20** (2000) [4] 297–302

[8] Kendall, T.: Recycling of refractories, what price waste? Industrial Minerals (1994) [323] 32–40

[9] Report "Critical Raw Materials for the EU". Report of the Ad-hoc Working Group on Defining Critical Raw Materials. EU-Commission, DG Enterprise and Industry, Brussels, 2010

[10] Morii, H.; Kinoshita, H.; Adachi, S.: Reusable sliding gate plate. Proc. of Unified Int. Technical Conf. on Refractories (UNITECR 2011), CD, Kyoto, Japan, 30. Oct.–2. Nov. 2012