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High Purity Composite Briquette for Direct UMG-Si Production in Arc Furnaces

Raymond Perruchoud* and Jean-Claude Fischer
R&D Carbon Ltd
P.O. Box 362, ,CH-3960, Sierre, Switzerland

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In the Metallurgical Grade Si (MG-Si), the B and P contents are in average above 30 ppm as the carbon reduction materials used in the arc furnace are either rich in B (coal) or in P (charcoal). A decrease of both impurities by a factor 3 by using purer raw materials would allow the direct production of the Upgraded Metallurgical Grade (UMG).This would significantly improve the efficiency of the resulting PV cells made with the refined Solar Grade Silicon (SoG-Si) or decrease massively the costs of Si purification by shortening the number of steps needed for reaching B and P contents below 1 ppm requested for the SoG-Si used for the PV cells.

A composite C/SiO_2 briquette fulfilling the purity targets for the direct production of UMG-Si in arc furnace was developed. The composite contains several carbon materials with different levels of reactivities and quartz sand. The raw materials aspects, the paste and briquette preparation, as well as the final carbonization step are commented. The finished briquettes are free of volatiles and are mechanically and thermally very stable, thus ensuring stable arc furnace charges with minimum losses of dust and SiO gas. Semi-industrial trials including the downstream purification steps for the production of SoG-Si by a metallurgical low cost route are contemplated.

Keywords: Photovoltaic cells, metallurgical silicon, arc furnace, raw materials.

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* Corresponding author E-mail address: info@rd-carbon.com

Композитные брикеты высокой чистоты для прямого производства металлургического кремния глубокой очистки в дуговых электропечах

Раймонд Перручоуд, Жан-Клод Фишер
R&DCarbonLtd
Швейцария, 3960 Sierre, а/я 362

В металлургическом кремнии (MG-Si) содержание B и P в среднем превышает 30 ppm, так как в применяемых в дуговых печах материалах, восстанавливаемых углеродом, содержание B (уголь) или P (древесный уголь) высокое. Уменьшение содержания обеих примесей в три раза при использовании сырья более высокой чистоты могло бы обеспечить прямое производство металлургического кремния глубокой очистки. При этом существенно повысится эффективность солнечных батарей, изготовленных из кремния солнечного качества, произведенного по данной технологии рафинирования, благодаря уменьшению количества этапов, необходимых для снижения содержания B или P ниже 1 ppm, в соответствии с требованиями к кремнию солнечного качества, используемому для производства солнечных батарей, снизится стоимость очистки Si. Композитный брикет C/SiO$_2$, отвечающий требованиям чистоты, разработан для прямого производства металлургического кремния глубокой очистки в дуговой печи. Композит содержит кварцевый песок и несколько углеродных материалов с различными уровнями реакционной способности газа и кварцевого песка. Рассматриваются некоторые аспекты сырьевых материалов, подготовки массы и брикетов, а также окончательный этап карбонизации, проведенной в вертикальной ретортной печи. Готовые брикеты не содержат летучих, отличаются высокой механической и термической устойчивостью, что обеспечивает стабильность загрузки дуговой печи с минимальными потерями пыли и газообразного SiO. Рассматриваются результаты полупромышленных испытаний, включающих последующие этапы очистки для производства кремния солнечного качества по металлургической схеме наименьшей стоимости.

Ключевые слова: фотоэлементы, металлургический кремний, дуговые электропечи, сырьевые материалы.

From metallurgical Si to photovoltaic cells

The reduction of quartz raw materials with carbon materials in arc furnaces delivers MG-Si with purity close to 99% (2N). The efficiency of PV cells is among other things strongly influenced by the P and B contents of the Si.

The figure 1 shows that it reaches a maximum plateau for concentrations below 0.1 ppm. Therefore downgraded electronic Si (8N to 6N) was, and is still, used for PV applications. UMG-Si is not competitive as the loss in efficiency exceeds 10% rel. but remains the preferred feedstock for the preparation of SoG-Si (better than 6N) by using a metallurgical refining low cost route.

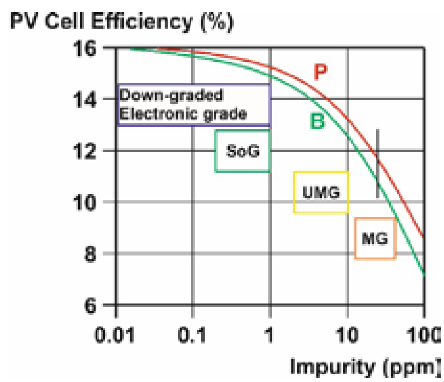

Fig.1. B and P impact on the cell efficiency. Redrawn from [1]

Where are P and B impurities in the MG-Si coming from? Beside the 2.5 tons of quartzite containing some ppm of P, the arc furnace process requires about 1 ton of several carbon reduction and electrode materials. Up to six C containing materials can therefore be used namely, woodchips, charcoal, coal, petcoke and anthracite based paste with graphite core electrodes.

The wood and charcoal are rich in P while the coal based products are rich in B. The level of P loss from the carbon reduction materials reaches 90%. From the quartzite, melting only in the lower hot part of the furnace, the P loss is unfortunately lower (about 50%). More than 90% of B present in any raw materials is found in the metal [2].

The metallurgical route of purification during cooling of liquid Si involves segregation of impurities by directional solidification. This works not very well for P and B for which the coefficients of segregation (the ratio of concentration in solid versus the one in liquid) reach high values close to 1. At least one refining step is therefore needed with typical MG-Si for lowering their concentration below 10 ppm to obtain UMG-Si, the feedstock of the SoG-Si.

Petroleum based coke material would be ideal reduction material from a purity point of view, but its amount in the charge is limited to some percent only, due to the lack of reactivity to SiO gas [3] or to liquid SiO_2 for the formation of intermediate SiC prior its transformation to Si [4].

An excess of low reactivity carbon leads to poor efficiency and high energy consumption as well as to furnace operation difficulties. However higher percentage of such low reactivity carbon have been used successfully, providing intimate contacts with finely distributed quartz favour the reaction rates. This intimate contact means a production of composite briquettes with relatively fine quartz sand which is bounded with a suitable organic material, a concept already used in the eighties that was revisited and eventually improved by using the state of the art technologies for paste and carbonized briquettes preparation.

Behaviour of composite C/SiO_2 briquettes in furnaces

Conventional charges components

With conventional lumps of quartzite the selection of the carbon blends is made according to the reactivity to SiO as high reactivity carbons trap the SiO in the outer zone of the furnace by transforming it into SiC. High reactivity being correlated with the porosity of the carbon material the preferred source is charcoal as during the carbonization of the wood more than 85% of volatiles create a maximum of pores. Chars from non-coking coal (40% of volatiles) have also an interesting high reactivity, but metallurgical cokes from coking coal and especially petroleum cokes are far less porous and therefore show low reactivity to SiO.

Reaction mechanisms with composite briquettes

It is astonishing that briquettes with calcined coke materials from coking coal, green coke and coal tar pitch (Ancit briquettes) were operating well. From one side the faster melting of the fine quartz together with the intimate contact with the carbon components is quickly producing the needed SiC in the intermediate zone of the furnace. Another possible explanation is that the preferred reaction involving SiC and liquid SiO_2 in the inner hottest zone is the one producing no SiO but only Si, namely the reaction 5* as shown in the Fig. 2.

It was also observed that the reaction volume of the charge was much larger with briquettes, so that the velocity of the off-gas through the charge channels was reduced. Last but not least, the homogeneity of the charge was massively improved as the homogenization of the several raw materials having much different bulk densities and granulometries by simple stocking vehicle was, and remains, a tedious operation step.

Therefore less SiO reactive carbon components can do a correct job in term of efficiency and energy consumption. The ideal reaction sequence of briquette components for a 100% yield is shown in Fig. 2. The composite briquette still contains a relatively porous (Cp) and reactive carbon reacting with SiO but also an equivalent part of more dense carbon (Cd) that will react with SiO_2 later in the intermediate zone. The formed SiC will react with liquid SiO_2 from the molten lump quartzite in the lower inner part of the arc furnace.

Carbosil Briquette Process

The strength and weakness of the raw materials and process used in the past (Ancit and Silgro industrial briquettes) were revisited and a composite briquette concept, delivering a product named *Carbosil*, was developed. Emphasis was given in producing a briquette that is maintaining its strength and integrity during the transformation process related to the formation of SiC, from C reacting with the SiO oxidant gas or later with SiO_2.

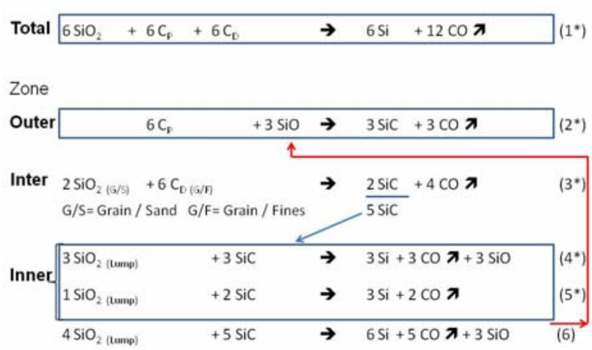

Fig. 2. Possible reaction sequences with composite briquettes and quartzite lumps [4]

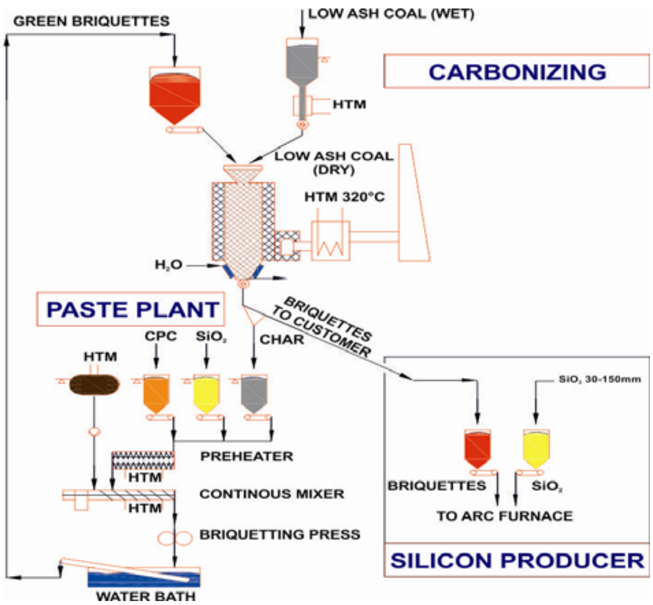

Fig. 3. Carbosil plant flow sheet

The original idea of the patented concept [5] is the co-carbonization process where the green briquettes are smoothly carbonized in a vertical retort together with one or more granular green carbons that will serve as carbonized raw materials for the production of the paste. The flow sheet shown in Fig. 3 shows the cycle process where eventually the finished briquettes are separated from the granular carbon by sieving.

Carbosil Pilot Composite Briquettes

Pilot plant and testing tools (Fig. 4)

The green granular carbons are carbonized preliminarily in a vertical pilot retort at a final temperature close to 750 °C. The carbon dry aggregate is prepared by crushing, sieving in continuous pilot roller crushers and multi-decks sieving machine. The most important step, which is the fines preparation, requests an air jet collision mill equipped with an air classifier for controlling the fineness.

The batches of dry aggregate recipe are preheated before mixing in an intensive propeller mixer. The paste is cooled by water addition to the right temperature before the pressing of 20 cm^3 briquettes. The green briquettes are co-carbonized with the corresponding amount of green materials that are later integrated in the manufacture of the green briquettes.

Physical characteristics of Carbosil briquettes

The Table 1 shows the results of briquettes of similar dimensions and geometry with a level of C/SiO_2 weight ratio of 1 corresponding to a molar ratio of 5. The apparent density of the *Carbosil* composite briquette is the highest and its load strength reach unprecedented high levels thanks efficient mixing of the optimized dry aggregate mainly.

Fig. 4. Pilot Plant equipment for *Carbosil* briquettes

Table 1. Comparison of *Carbosil* to previous industrial briquettes (Ancit and Silgro)

Properties	Unit	ANCIT	SILGRO	*Carbosil*
Apparent density	Kg/dm^3	1.49	1.35	1.52
Load strength	Kg	120	80	140
Loss in CO_2	%	14	18	13
Dust in CO_2	%	11	54	9
Ratio loss / dust	-	1.2	0.3	1.4
Volatiles	%	4	6	3
Non SiO_2 ash	%	3	2	0.2

The most encouraging data is the low selective burning and good integrity of the briquettes after the CO_2 reactivity test. The ratio loss to dust of the *Carbosil* briquettes reaches 4 times the Silgro value and is superior to the Ancit briquettes used with good success in the past.

Impact of *Carbosil* on the Si metal purity

B and P from the charge components into the metal

Boron oxides show boiling point above 3000 °C so that the majority (90%) of the incoming impurity will be transferred into the metal. For P different distributions were observed as its volatility from the carbon reduction material is as expected high (10% only in Si metal), but intermediate (50%) for the P impurities integrated in the large size quartzite lumps reacting only in the inner zone of the furnace.

Conventional charge situation for B and P in the MG-Si

For a comparison basis we can consider the production of MG-Si where raw materials purity and charge composition are selected in such a way to get an equal contamination of B and P in the metal.

The Tables 2 and 3 show that due to the high content of B in coal or char and of P in charcoal a blend of carbon raw materials is mandatory.

With charcoal, coal and char as main reduction materials in conventional charges a content of 35 ppm of both elements B and P is found in the MG-Si metal. With such a high level of these critical elements for the efficiency of the PV cells little can be done in the selection of more expensive purer raw materials so that emphasis remains the selection of cheap raw materials for the MG- Si producer. This means much higher refining costs for the SoG-Si preparation.

Carbosil composite briquettes in the charge

The maximisation of petcoke content, which is much higher than in the in the conventional charge and this without operation and yield drawbacks, is decisive for reducing the contamination of both elements B and P. With this scenario of 2 tons of *Carbosil* (one ton each of C and SiO_2) together with

Table 2. Raw materials characteristics in conventional charges

Raw materials	Moisture, %	Ash, %	Dry basis	
			B, ppm	P, ppm
Charcoal	5	2	5	140
Coal	10	1.5	40	10
Char	5	2	60	15
Green coke	10	0.5	3	5
Woodchips	33	1	1	60
Electrode	0	2	10	10
Quartzite A	0	0.8*	2	10

* non-SiO_2 oxyde

Table 3. B and P in Si metal with conventional charges

Components	Kg/t Si	Ash, %	B, ppm	P, ppm
Charcoal	600	1.2	3	133
Coal	300	0.4	11	3
Char	300	0.6	17	4
Green coke	50	0	0	0
Woodchips	2000	2	2	80
Electrode	100	0	1	1
Σ from C materials		4.2	33	221
% in Si metal			90	10
In Si from C materials			30	22
From Quartzite A	2500	2.0	5	25
% in Si metal			90	50
In Si from Quartzite A			5	13
Total in Si			35	35

Table 4. Raw materials characteristics with *Carbosil* in the charge

Raw materials	Moisture, %	Ash, %	Dry basis	
			B, ppm	P, ppm
Coal washed	10	0.5	10	5
Green coke	10	0.2	2	3
Coal tar pitch	0	0.2	3	3
Woodchips	33	1	1	60
Electrode	0	0.5	2	3
Quartzsand	0	0.3*	0	1
Quartzite B	0	0.4*	1	5

* non-SiO_2 oxyde

Table 5. B and P in Si metal with *Carbosil* Briquettes

Components	Kg/t Si	Ash, %	B, ppm	P, ppm
Carbosil carbon	1000	0.5	8	5
Woodchips	1000	1.0	1	40
Electrode	100	0	1	1
Σ from Carbosil carbon		1.5	10	46
% in Si metal			90	10
In Si from Carbosil carbon			9	5
From Quartzsand	1000	0.3	0	1
From Quartzite B	1500	0.6	1	8
% in Si metal			90	50
In Si from Quartzite B			1	5
Total in Si			10	10

1.5 ton of quartzite, a contamination of 10 ppm only is obtained for both B and P elements (Tables 4 and 5).

The Si metal metal produced with the *Carbosil* briquettes, with 3 to 4 times less B and P than with conventional charges, meets the requirement of UMG-Si. The purity of the produced Si reaches 99.8%.

The refining costs needed for reaching the threshold below 1 ppm specified for the SoG-Si are therefore massively reduced.

Conclusions

In the race towards cost reduction of PV cells below 1$/Wp the direct production of UMG-Si in arc furnaces using high purity *Carbosil* briquettes plays an important role. A better purity of the SoG-Si, meanings a higher PV efficiency, reduces the investment costs and can bring the electricity generation to a competitive level for large scale power plant.

The pilot scale works on these high purity briquettes have resulted in a plant basic design that can be fine tuned after semi-industrial trials have been performed.

The ideal partner embarking into such a project is a metallurgical Si producer having already developed a metallurgical refining route for the preparation of SoG-Si, a partner that is naturally eager to lower the refining production costs and to expand its production.

The collaboration with world class coal washing plants and high purity quartz sand producers can be contemplated as well. The access to an appropriate paste carbon plant remains mandatory for the validation phase where semi-industrial lots are tested and is a must for a smooth industrialization of the composite briquettes dedicated to the production of UMG-Si, the ideal feedstock for a low cost SoG-Si production.

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