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# SILICON FOR SILICONES : A DEVELOPING ROUTE FOR P.E.M

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## ABSTRACT

Aimed at developing a silicon grade to match the needs of silicone industry, PEM initiated a work programme several years ago, in order to identify the significant parameters of silicon which will permit the direct synthesis reaction to be optimised and to transfer into the production process the results of the research.The role of the process on quality parameters forms the subject of ongoing research work, permitting optimum conditions for process operation to be determined.

Such research work is being conducted thanks to collaboration between the various departments within the company: R&D, technology, production, as well as through efficient technical cooperation with the customers.

The purpose of this article is firstly to recall the main investigated research paths, as well as to detail the main parameters which interact in the application and the available means of action to control them. Then, a description is given of late developments of production means implemented to stabilize the complete process and to enable the production of the silicon the best suited to each customer.

## KEY PARAMETERS IDENTIFICATION

For this purpose, the studies are broken down into 3 areas : the product, the production method, the application.

Research studies were conducted at our in-house research centers as well as in cooperation with Public research organisations and our customers.

### Product studies

Product studies involved the various components of silicon:
- -primary silicon: grain size, structure and physical defects,
- -intermetallic phases: composition, physical characteristics and behaviour in direct synthesis.

### Studies on silicon properties in direct synthesis

The studies were carried out in cooperation with the customers or in the scope of subcontracts to university laboratories.

## Process studies

The results of the above studies enable the objectives of the work required to be determined in order to achieve silicon process evolutions permitting a silicon better suited to our customers' needs to be obtained.

# NATURE OF INTERMETALLIC PHASES

## Intermetallic phases in silicon

The first step of the study consisted in determining the nature of the various intermetallic phases likely to be found. Results were described previously [1-8] by PEM and various authors. It should be noted that the following main phases can be found:

$FeSi_{2,4}$, $CaSi_2$, $CaSi_2Al_2$, $FeSi_2Al_3$, $Fe_4Si_6Al6$, $Si_8Al_6Fe_4Ca$ (quaternary phase).

Intermetallic phases contain also secondary impurities, some of which concentrating preferably in a given phase.

## Controlling intermetallic phases nature

The properties of these intermetallic phases in direct synthesis are not the same [9] hence it is necessary to know the rules which govern the nature of said phases in silicon.
A first descriptive approach had led to proposing an experimental diagram for a restricted area of composition [2]. A more complete approach is described hereinafter.

## Phase diagram

Phase diagram calculation [1] was used to evidence the phases present at equilibrium.
Based upon the equilibrium diagram, a simplified diagram was proposed [3] and developed against the acquired experience, in order to account for non-equilibrium states (Figure 1).For a quaternary system, the stability field at a given temperature should be represented by a tetrahedron with apices Si, Fe, Al, Ca. Figure 1 shows a section of this tetrahedron across a plane of constant Si content. The nature of the phases observed in a silicon is deduced from the position of the representative point of its composition in this section.
In addition to the areas where equilibrium phases are found, Figure 1 also shows the regions where the Si2Al2Ca and FeSi2Al3 phases can be present under non-equilibrium conditions.

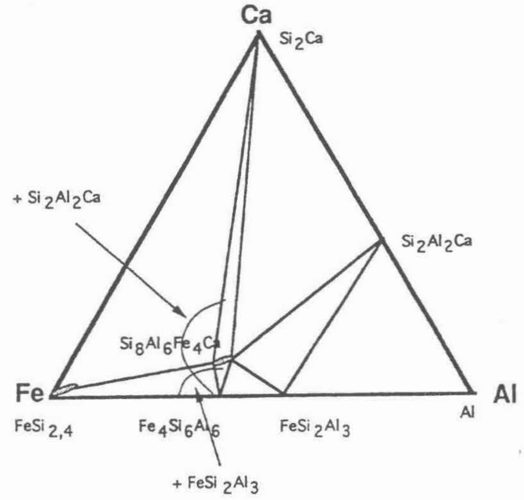



Fig. 1 Section of constant Si composition through the Si tetrahedron showing the phases observed at 500°C

## Non-equilibrium states

The detailed study of precipitation mechanisms shows that during solidification, certain phases appear temporarily and disappear as equilibrium conditions are met. These phases persist when cooling is rapid, and the number of phases is then more than expected under equilibrium conditions ( phase diagram [3-4]).
This accounts for the phenomena observed experimentally.

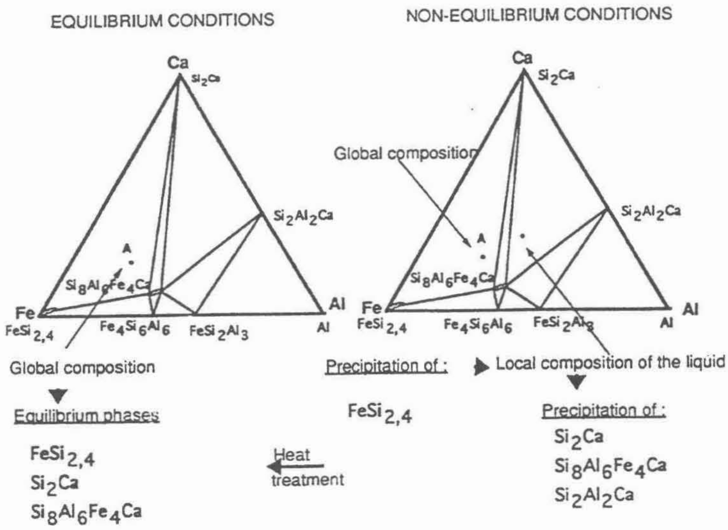



fig 2 : Description of precipitation of the intermetallic phases under non-equilibrium conditions

The significant result to be highlighted is that solidification speed affects the nature of intermetallic phases for a given composition.

## Conclusions on the nature of intermetallic phases

The prevailing parameter which determines the nature of intermetallic phases is composition in secondary elements under metallic state in the liquid at the time of solidification. To obtain a silicon featuring constant characteristics against intermetallic phases, it is therefore necessary to ensure consistency of the composition by acting on raw materials, refining and pouring conditions.

The second major parameter is solidification speed which will affect the nature of intermetallic phases for a given composition.

## STRUCTURE OF THE SILICON

Several interrelated aspects should be considered:

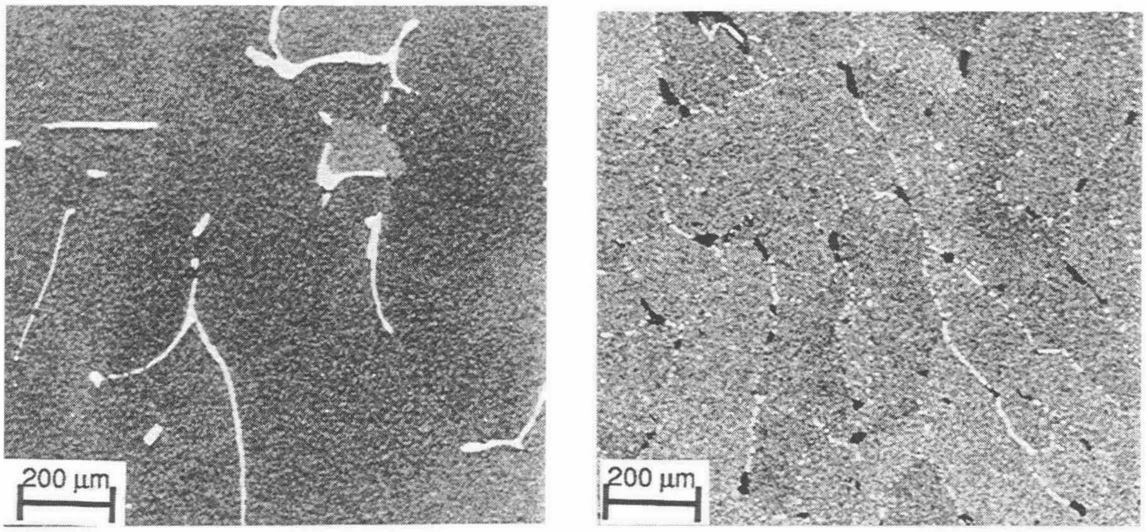
- intermetallic grain size
- silicon grain size
- intermetallic phases distribution

These parameters are essentially dictated by solidification conditions.

## Silicon grain size and intermetallic phases distribution

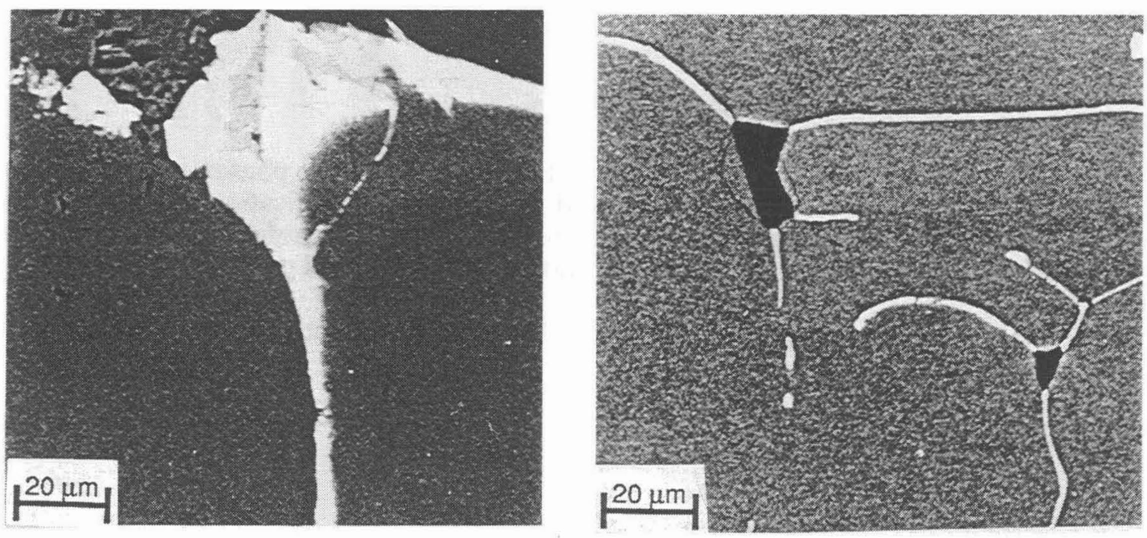
Intermetallic phases precipitate from a liquid containing about 50% impurities. This implies that the onset of precipitation of the intermetallics should occur when only about 1 % of liquid remains: intermetallic phases distribution is determined by silicon crystal size and these two parameters are correlated.

The effect of solidification speed is shown on the images in Figure 3: Two silicons featuring the same composition are compared: one is solidified as an ingot, the other is obtained by water granulation. The images were taken by electronic scanning microscopy.
High solidification speeds lead to smaller silicon grains hence a more scattered intermetallic phases distribution.




3a 3b

Fig. 3 Intermetallic phases distribution in silicon: normal cooling (3a) - Fast cooling (3b) - Back scattered electron image (BSE)




4a 4b

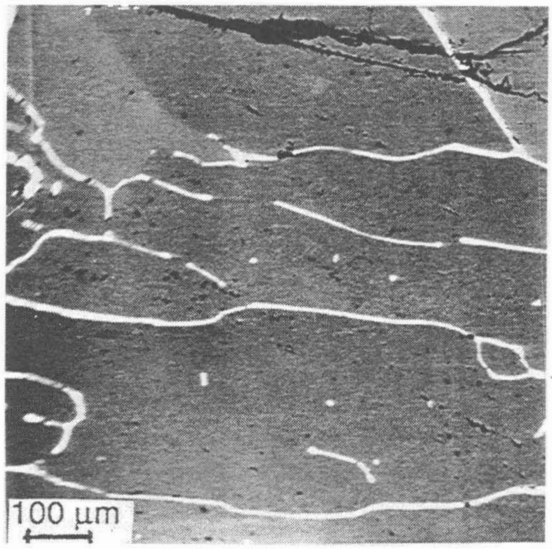
Fig. 4 Intermetallic area in silicon: normal cooling (4a) - Fast cooling (4b) - Back scattered electron image (BSE)

## Intermetallic grain size

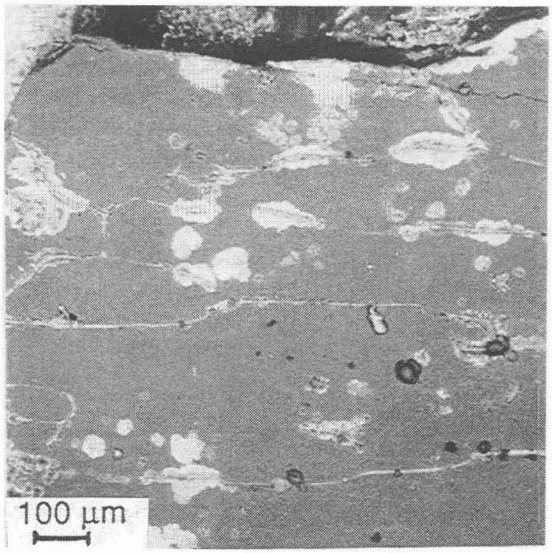
For a given analysis, the intermetallic phases proportion is constant: in parallel, a more scattered distribution of intermetallic phases leads to a thinner grain size. This evolution is detailed in Figure 4 for the same samples.

## Intermetallic structure role

It can be noted that intermetallic phases are initial attack sites for the chloromethylation reaction. Figure 5 illustrates this behaviour [9]. The number of such sites is determined by the length of the silicon grains associated with intermetallics. Hence it increases in line with solidification speed.




5a




5b

fig.5: Silicon before (5a) and after (5b) methyl-chloride reaction

## Intermetallic phases distribution quantification

Image analysis permits the intermetallic phases distribution to be quantified, as well as indirectly, the silicon grain size.

The following method was implemented:

-digitising the images obtained under electronic microscope,

-measuring the intermetallic surface area,

-applying an expansion treatment by adding a given pixel thickness to the initial surface and measuring the new surface area thus obtained. This operation is repeated n times and the surface evolution versus the number of expansion treatment operations depends on the total length of the intermetallic phases. This evolution is compared on Figure 6 for a silicon solified as an ingot and a water-granulated silicon.

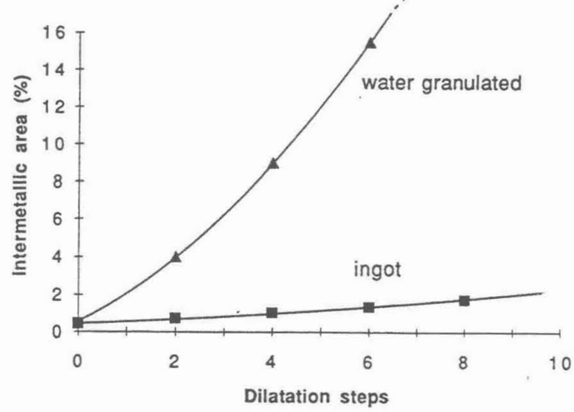



fig 6 :evolution of the intermetallic surface versus the number of expansion treatment operations for two cooling conditions

The ratio between the surface area obtained after a given number of expansion operations and the initial surface area enables the intermetallic structure to be characterised; in the previous example, it demonstrates that granulated silicon features a grain boundary length with intermetallic phases ten times longer than silicon solidified in ingot form.

## Physical crystal structure

Some physical characteristics of the crystal are variable.
Twins: their size, for a given analysis, essentially depends on solidification speed. At the milled grain surface, it results in punctual defects (sharp edges) which make up preferential attack sites [9-10].

Dislocations: this physical defect of the crystal is caused by various mechanisms:

- high solidification speed,
- presence of precipitates
- proximity of a grain boundary

## Impurity content:

Direct analyses by physical methods demonstrated that the metallic aluminium content in the crystal depends on solidification conditions. Other elements are currently being studied.

## OXYGEN

The main 3 forms of oxygen in silicon are:

-oxygen dissolved in the crystal: the Si-O diagram (Figure 7) gives the values at equilibrium. Higher values were observed, accounting for supersaturation phenomena.

-surface oxygen: it is essentially introduced at the time of milling; Figure 8 illustrates the relationship between surface oxygen and the specific surface area of the powder obtained under industrial conditions. These values are consistent with those indicated by RONG [8].

-inclusions: Oxide inclusions found result from various mechanisms which determine their nature and quantity:

.oxygen is present in submicronic inclusions of silicon carbide, under the form of alumina;

.the essential part of the inclusions comes from slag poorly separated during refining and pouring. It presents highly variable sizes. In fact, it is calcium silico-aluminate either containing SiC or not. Its composition is determined by the furnace operating mode, the refining conditions (oxygen quantity, temperature) and the pouring technology.
An example of inclusion composition likely to be found for a given process is illustrated in the diagram Figure 9.

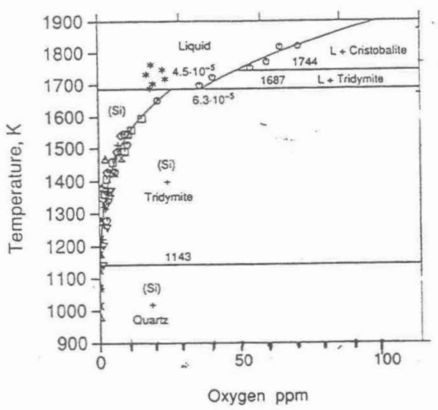



Fig. 7 Silicon oxygen equilibrium diagram [11]

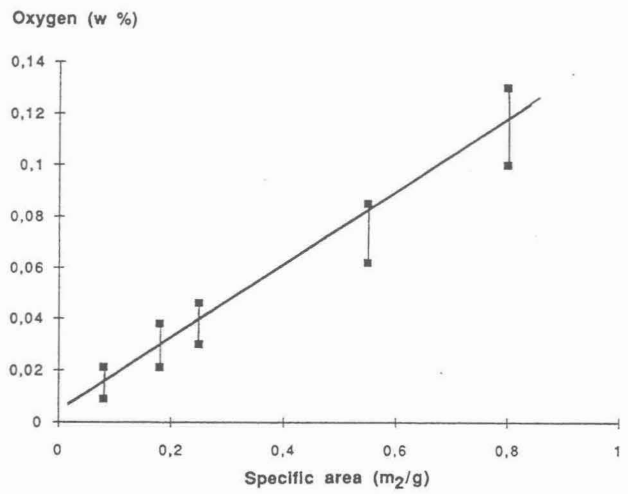



Fig. 8 Relationship between surface oxygen content and the specific surface area of a silicon powder

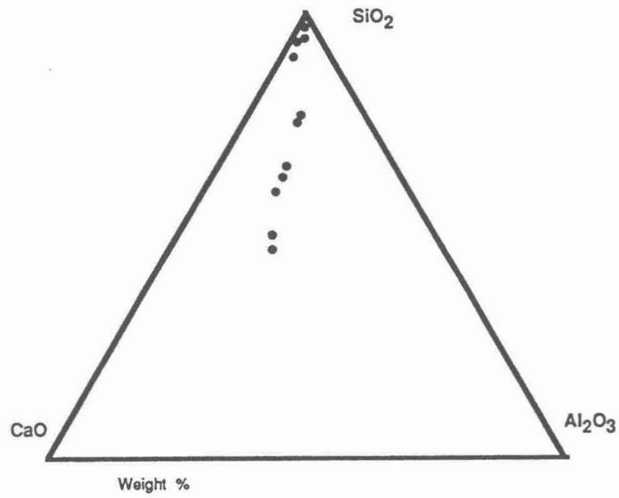



fig. 9: Composition of slag inclusions found in ingot silicon for a given refining process

These characteristics allow the mechanisms at the origin of the slag contamination to be determined, and therefore, permit process corrections to be implemented to minimise the contamination.

## Role of oxygen

Oxygen is involved in various manners:

-if slag is present, part of the metallic impurities is oxidised and therefore the bulk analysis fails to characterise the product accurately,

-it causes accumulation of inert products in chloromethylation reactors.

## Conclusion regarding oxygen

All process stages are involved in the possible introduction of oxygen into silicon. A good understanding of the various forms of oxygen and of the introduction mechanisms enables us to develop processes for obtaining silicon with minimum oxygen content.

## SILICON CONSISTENCY AND PROCESS OPTIMIZATION

One of the major characteristics of high quality silicon is consistency. PEM has developed and implemented in its production plants, controls to stabilize the entire process resulting in a very consistent product.

### Furnace operation

In order to optimise furnace performance and improve operation consistency, PEM focused its efforts on the choice of raw materials: industrial tests, characterisation, quality control, as well as on the furnace follow-up and control modes.

In this last field, we have followed at the same time two convergent paths, leading to a common result:

- -development of expert systems to collect and then reuse specialists' experience and knowledge in the various control situations,
- -development of graphic and digital follow-up indicators based upon the most accurate knowledge achievable, concerning silica and carbon material balances.

The combination of those two approaches gives now to the operators the means to implement the required actions to obtain satisfactory performance levels and stabilise them.

This better control has enabled PEM to increase the power of the furnaces which went from an average installed power of 13,5 MW in 1987 to an average power of 19,5 MW in 1994 whith 5 furnaces over 20 MW in the three plants of Anglefort, Montricher and Les Clavaux where a 23 MW furnace was started up in 1992.

### Refining

The silicon refining techniques evolved and became much more accurate, in order to achieve the targeted Al and Ca contents, with the least possible spread effect.
The objective is to reach maximal success rates in targeted grades, which are themselves determined by more and more stringent limits, product consistency being the prevailing quality parameter.

This evolution is effective both as regards refining by the top of the ladle, by means of a graphite tube, and refining by the bottom of the ladle, by means of a nozzle.
These enhancements were made possible by PLC control of the refining parameters (flows, pressure, duration, temperatures, additions) as well as by the development of expert systems which automatically modify the refining parameters and propose corrective and checking actions to the operator, as a function of the results of previous ladles analyses.

### Inclusion quality

Quantitative and qualitative checking for the presence of oxygen in the silicon enables the quantification of the effect of various methods likely to be used, in order to improve the inclusion quality of the silicon and therefore to fine-tune the refining and pouring techniques.

The industrial tests which led to systematic applications or not, involve the following:

- -temperature control,
- -slag composition,
- -pouring technique
- -decantation,
- -filtration.

## Solidification

For a given solidification method, the equipments enable to guarantee a consistency of cooling conditions and therefore of silicon structure.
It must be added that PEM is equipped with a wide range of casting and solidification equipment, permitting different cooling rates and hence diversified crystalline structures.

By increasing order of solidification rate, we can produce:
- 700 kg ingots, 15 to 20 cm thick,
- 30 kg ingots, 5 to 10 cm thick, uncooled
- 30 kg ingots, 5 to 10 cm thick, water-cooled
- water granulated silicon, 1 to 12 mm diameter.

The latter method directly produces ready to mill grains, featuring fine crystalline structure and homogeneous composition. It required heavy investment and long and intricate adjustments.

## Milling

PEM delivers silicon to certain customers in the form of powder, directly usable in their reactors. A specific effort is done in order to provide these customers with a product offering best behaviour in fluidisized bed.
It is necessary to produce the closest possible grain size distribution.

## Quality Assurance

The platform of three silicon plants together with the marketing department and the division management board are certified to ISO 9002.

All work methods are described in procedures, strictly applied by all collaborators.
Singleness in practices is another element permitting product steadiness to be ensured, which is essential for utilisation by industrial silicone users.

The follow up of the various parameters used to control the different steps of the production process, is largely, based on the use of SPC control methods.

# CONCLUSIONS

The various physical and chemical characteristics of silicon which affect direct synthesis significantly were studied in detail:

- nature of intermetallic phases,
- intermetallic phase morphology,
- silicon-crystal characteristics,
- secondary impurities, in particular oxygen.

Each silicones manufacturer has its own reactor adjustments and catalytic system. The best suitable silicon for a given application corresponds to an ideal chemical analysis and structure combination. This combination should be determined in close collaboration between the silicon producer and the silicone manufacturer.

PEM has equiped its three silicon plants with the modern production and control equipements essential for the stabilization of the complete process and for the production and delivery to its customer of a silicon of great consistency the best suited to each application.

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