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Intermetallic Compounds in Metallurgical Silicon

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Metallurgical silicon is manufactured in industrial furnaces from quartzites and various carbonaceous reductants containing metallic impurities that provide up to 1 per cent of the silicon metal. These metallic impurities, which are compounds of silicon concentrated at grain boundaries, induce precipitates in metallurgical silicon during solidification.

By scanning electron microscopy with wave-length-dispersive X-ray analysis, we identified up to ten binary, ternary, and even quaternary compounds.

In this way, intermetallic compounds in the silicon-rich zone were studied as to their physical and chemical properties. They are Si_2Ca, Si_2Al_2Ca, $Si_8Al_6Fe_4Ca$, Si_2FeTi, $Si_7Al_8Fe_5$, Si_2Al_3Fe, and $Si_{2,4}Fe(Al)$.

According to the ratio of contained impurities, we established the existence area of each compound in metallurgical silicon for a given cooling condition. We calculated the equilibrium phase diagrams to understand the mechanism of solidification. Some experiments showed good agreement between calculated and experimental values. To define a better production method for silicon, we examined the influence of intermetallides on the chloromethylation reaction.

Experimental data showed the influence of cooling conditions on the stability field of intermetallides. For example, the annealing of silicon at around 900 °C increases the amount of quaternary intermetallic $Si_8Al_6Fe_4Ca$ while destroying the ternary Si_2Al_2Ca according to the reaction

$$3\ Si_2Al_2Ca + 4\ Si_2Fe \rightarrow Si_8Al_6Fe_4Ca + 2\ Si_2Ca + 2\ Si.$$

A knowledge of the phase diagrams and of the non-equilibrium reactions that occur gives rise to an understanding of the mechanism of solidification and, consequently, the behaviour of silicon for any composition and cooling condition.

Knowledge of the silicon structure and of the parameters governing this structure leads to an understanding of the behaviour of silicon and of ways to modify its properties, the purpose being the optimization of its use in many applications.

Metallurgical Silicon

Industrial silicon is obtained by the reduction of silica by carbon:

$$SiO_2 + 2\ C \rightarrow Si + 2\ CO \quad \triangle H = 880\ kJ/mol.$$

This reaction takes place in a submerged-arc furnace at the tips of the electrodes at a temperature of about 1900 °C, and involves many sub-reactions.

The raw materials used to produce 1t of silicon are as follows:

Silica	Quartzite or pebbles	2 500 kg
Carbon	Low-ash coal	800 kg
	Petroleum coke	200 kg
	Wood chips	1 200 kg
	Carbon electrodes	90 kg.

The electrical energy required is 11 000 kWh.

Characteristics

The raw materials contain impurities, some of which are transferred to the silicon. The silicon has the following typical analysis as tapped (in percentages by mass):

Si	98,5
Fe	0,3
Al	0,4
Ca	0,6
Ti	0,03.

(All the compositions in this paper are reported in percentages by mass.)

A refining treatment of the liquid silicon enables the desired concentrations of Ca and Al to be achieved depending on the end application. The material is crushed after solidification.

Uses

Silicon as an alloying element for light aluminium alloys needs low contents of Ca, Fe, and P.

The first step in the synthesis of silicones is the production of methylchlorosilanes by the reaction

$$\mathrm{Si} + 2\,\mathrm{CH_3Cl} \xrightarrow[\text{Catalyst}]{300\ ^\circ\mathrm{C}\ >} (\mathrm{CH_3})_2\,\mathrm{SiCl_2} \text{ and co-products.}$$

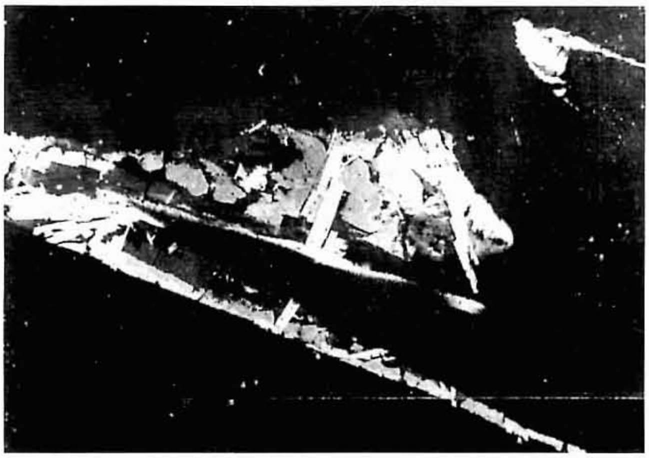
This application requires a precise content of Ca and Al, depending on the operating conditions. The impurities are concentrated in intermetallic compounds, which have a major influence on the reaction of chloromethylation.

Silicon as a raw material for semiconductor-grade silicon is transformed into trichlorosilane, which is used, after purification, to produce high-purity silicon.

Silicon is also used in the ceramic, welding, and steel industries.

Structure of Industrial Silicon

In order to determine the main parameters governing the properties of silicon, we studied its structure, and more particularly the intermetallides and their influence on the production of silicones.



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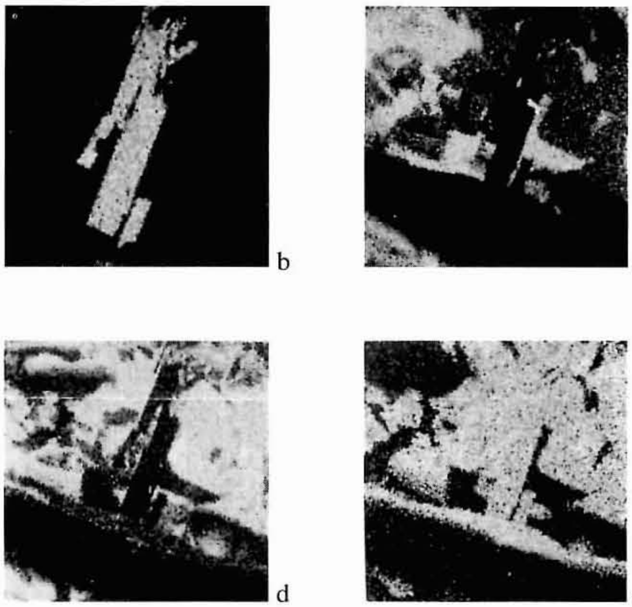

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FIGURE 1. SEM images of intermetallides in silicon Secondary electron image (a), X-ray images of titanium (b), X-ray images of aluminium (c), X-ray images of calcium (d), X-ray images of iron (e)

Methods of Analysis

The structure of silicon was studied by scanning electron microscopy (SEM), a method that can yield the following information:

- electron images with a contrast based on the average atomic number
- X-ray images showing the distribution of elements
- local analysis of phases.

Transition electron microscopy (TEM) and X-ray diffraction (XRD) were also used.

These studies were made on samples of industrial or synthetic alloys. For the phases that are not well known, trials were made on alloys enriched in Fe, Al, and Ca, and thermal analysis was used in the study of crystallization mechanisms.

The different intermetallides found are listed in Tables I and II.

TABLE I
MEAN CHEMICAL COMPOSITION (%) OF THE MAJOR INTERMETALLIDES OBSERVED IN INDUSTRIAL SILICON

Compound	Si	Al	Fe	Ca	Ti	Mn	Ba	Cu	Ni	P
Si_2Ca	66,8	0,6	0,1	32,2	0,02	0,01	0,05	0,12	0,02	0,05
Si_2Al_2Ca	40,2	39,0	0,05	19,80	0,05	0,00	0,08	0,03	0,03	0,8
$Si_8Al_6Fe_4Ca$	43,3	29,8	20,9	5,6	0,06	0,40	0,00	0,03	0,03	0,02
Si_2FeTi	49,6	0,6	24,8	0,05	24,60	0,30	0,00	0,05	0,00	0,01
$FeSi_{2,4}(Al)$	67,1	3,2	29,1	0,3	0,03	0,80	0,01	0,03	0,00	0,02
Si_2Al_3Fe	38,3	45,8	14,9	0,1	0,05	0,30				0,02
$Si_7Al_8Fe_5$	35,7	40,3	23,6	0,2	0,06	0,40				0,01

TABLE II
MEAN CHEMICAL COMPOSITION (%) OF THE MINOR INTERMETALLIDES OBSERVED IN INDUSTRIAL SILICON

Compound	Si	Al	Fe	Ca	Ti	Mn	Ba	Cu	Ni	P
Si(Ca,Cu,Al)	50	3	0,5	39		0,05	0,02	6	0,50	0,04
Si(Ca,Ba,Al)	64	20	0,0	9	0,6	0,00	5	0,40	0,05	0,06
Si(Al,Ni)	39	33	4		0,5				23	
Eutectic	12	83	1,5	0,06	0,4	0,02				

The Intermetallides in Silicon

The intermetallides occur at the grain boundaries of silicon, as shown in Figure 1. This structure is explained by the mode of precipitation of intermetallides. When silicon solidifies, very pure crystals with less than 0,05 per cent of impurities form first, and the amount of impurities increases in the liquid phase. When the liquid composition reaches a certain value, the impurities precipitate as intermetallic compounds.

Description of the Intermetallides

Intermetallide $FeSi_{2,4}$

Two structures can be observed in this compound (Figure 2):

- High temperature (above 937 °C): tetragonal cell with presence of vacancies in the iron sublattice.

  The formula Si_2Fe (1-x) (with x about 0,17) is also used.
- Low temperature: orthorhombic cell with the formula Si_2Fe .

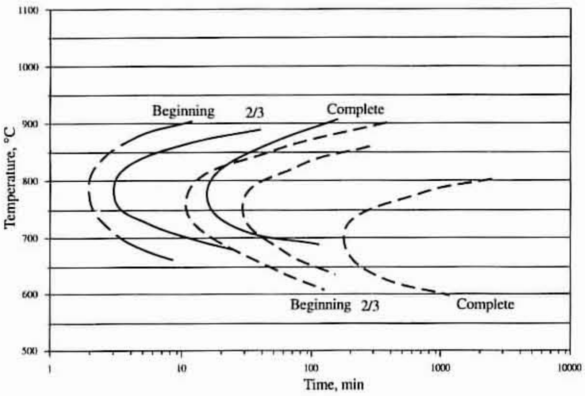

FIGURE 2. Isothermal transformation curves for $FeSi_{2,4}$
—— Without Al (the present work)
---- With[1] Al

With the standard cooling rates observed in the industrial production of silicon, the eutectoid transformation

$Si_{2,4}Fe \rightarrow Si_2Fe + 0,4\ Si$
does not occur.

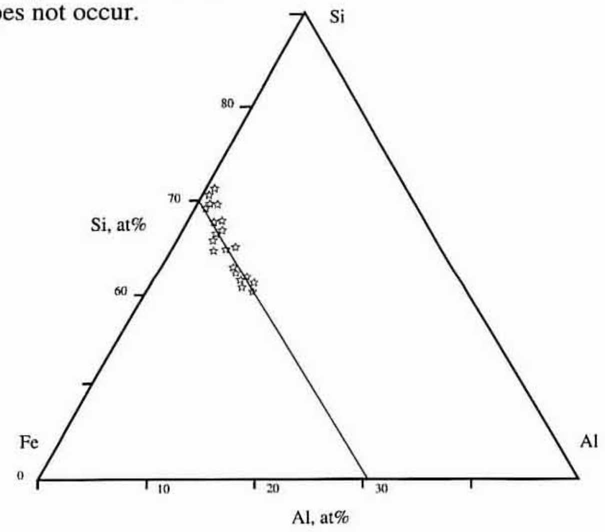

FIGURE 3. Composition range of $FeSi_{2,4}$ (Al)

By determining the rate of this reaction at different temperatures, we found that aluminium stabilizes the high-temperature structure. This phase can contain aluminium in variable amounts, depending on the silicon composition and the cooling rate (Figure 3). We can conclude that aluminium substitutes for the silicon atom (and does not fill the vacancies of the iron sublattice) in the structure of $FeSi_{2,4}$.

Intermetallide Si_2Ca

This compound can contain up to 2 per cent aluminium.

Intermetallide Si_2Al_2Ca

The phosphorus level may reach 1 per cent, and then this phase usually contains more than half of the total phosphorus content.

Ternary Phase Si–Fe–Al

Many phases can exist in the system, and some of them have a large compositional range, as we determined in additional studies. The compositional range of this system is shown in Figure 4.

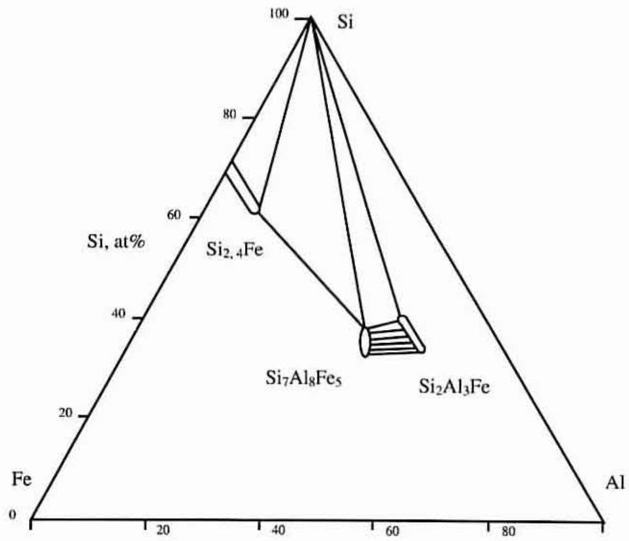

FIGURE 4. The compositional range of Fe–Si–Al

In industrial silicon, the two compounds Si_2Al_3Fe and $Si_7Al_8Fe_5$ occur, with analyses depending on the composition of the liquid.

Intermetallide Si_2FeTi

Most of the titanium is combined in the phase Si_2FeTi. In some cases, when the vanadium level is high, we also observe a phase containing V, Ti, and Si – possibly (Ti, V) Si_2.

Quaternary Phase

$Si_8Al_6Fe_4Ca$ is the only quaternary phase that can form in metallurgical-grade silicon, and many studies have been made of this phase. Different authors[1-5] have found compositions in the following ranges:

Si	Fe	Al	Ca
33,5 to 36	31,2 to 36,1	22,7 to 25,3	5,4 to 7,0 .

Thermal analysis of an alloy with a composition corresponding to the stoichiometry Si 8, Al 6, Fe 4, Ca 1 shows that the solidification is congruent.

Stability Fields of the Intermetallides

The number and kind of intermetallides present in silicon depend on its composition. The compositional range can be represented by a simplified diagram in which Fe is constant at 0,4 per cent and Ti is present in the form of Si_2FeTi. The composition is represented by a point in the Al–Ca diagram.

A study of about 30 samples of industrial silicon solidified at the same rate resulted in the diagram shown in Figure 5.

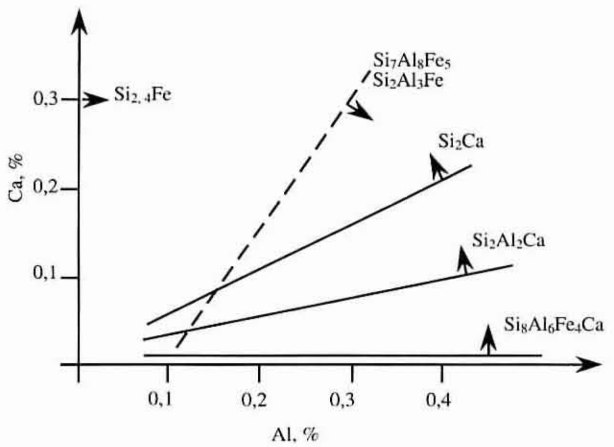

FIGURE 5. Compositional range of intermetallides in industrial silicon[6]

Industrial silicon contains more than 4 phases involving the elements Si, Ca, Al, and Fe.

A knowledge of the possible reactions (phases involved, and temperature), associated with experimental observations, allows the influence of the cooling parameters on the final structure to be predicted.

Method of Determination

As the experimental determination of a quaternary diagram is long and difficult, we decided to calculate it. The following steps were necessary:

- determination of thermodynamic parameters
- bibliographic and complementary experimental determinations (ethalpy of fusion for Si_2Al_2Ca, $Si_7Al_8Fe_5$, Si_2Al_3Fe, and $Si_8Al_6Fe_44Ca$)
- optimization of data.

The consistency of the data was controlled by a comparison between the experimental and the calculated values (phase diagram, activities, etc.). These studies had to be made for the six binary and the four ternary adjacent systems, and then for the quaternary system.

Results

Two calculated sections[5] are shown in Figures 6 and 7. In Figure 7 some experimental points are shown to indicate the good agreement between experimental and calculated values.

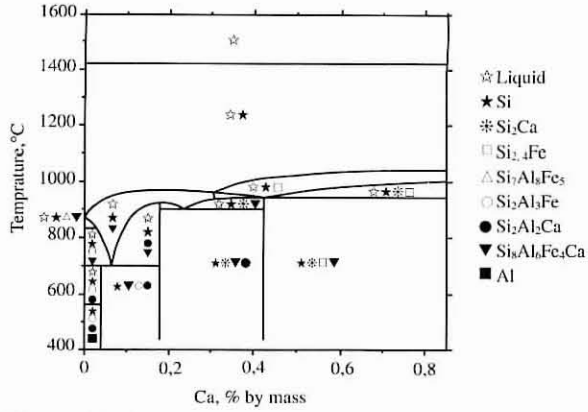

FIGURE 6. Section showing the Si–Fe–Al–Ca system calculated for Si = 99,2 per cent, Fe = 0,2 per cent, and Ca + Al = 0,6 per cent

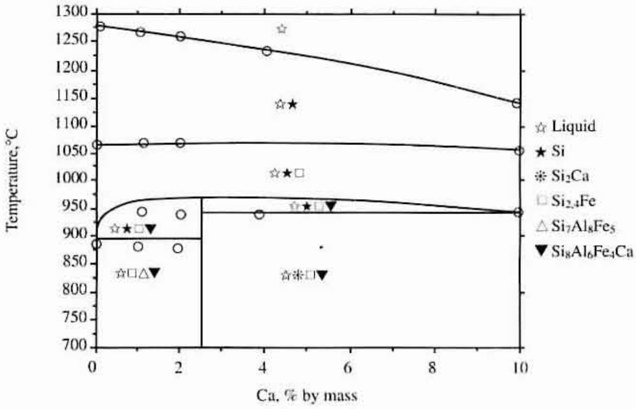

FIGURE 7. Calculated values (after Anglezio[5]) and experimental values (o) for an alloy containing Fe = 20 per cent, Al = 10 per cent, and Ca

An isothermal section at 500 °C is shown Figure 8.

In quaternary diagrams we must represent the stability fields at a given temperature of the phases in a tetrahedron with apices Si, Fe, Al, Ca. Figure 8 is a section of this tetrahedron across a plane of constant Si content. This diagram was deduced from the calculated sections shown in Figures 6 and 7.

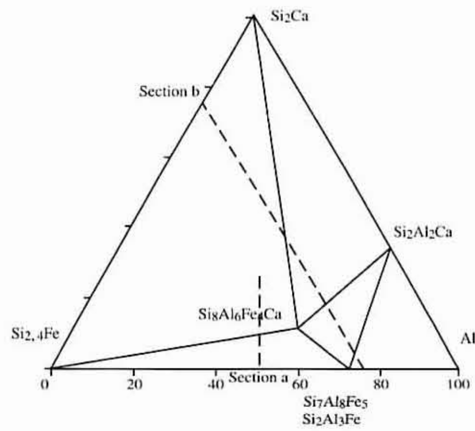

FIGURE 8. Section of constant silicon content through the silicon tetrahedron, showing the phases in equilibrium at 500 °C. The nature of the phases is marked by the projection on this section of their representative points in the tetrahedron. The broken lines correspond to the sections of Figures 6 and 7. This diagram agrees with the phase evolution in industrial silicon as described by the experimental diagram in Figure 5

Modification of the Stability Fields

The intermetallic compounds influence the properties of silicon, for example behaviour under the action of acid, safety properties (explosion hazard), and behaviour in the chlorosilane synthesis.

In regard to the role of intermetallides in chlorosilane synthesis, different methylchlorosilanes are obtained when CH_3Cl reacts on Si:

$$Si + 2CH_3Cl \rightarrow (CH_3)_2\,SiCl_2,$$

but only some of them are expected. The results of this reaction may be characterized by

- reactivity (related to the quantity of chlorosilanes produced per hour and per kilogram of Si)
- selectivity (the quantity of dichlorodimethylsilane related to the total of chlorosilanes).

In collaboration with a producer of silicones, we determined the role of the intermetallides, as shown in Figure 9. The exact influence of the different intermetallides depends on the technical conditions of the chloromethylation reaction, but it is important during the production of silicon to obtain a given distribution of intermetallides.

Composition	Selectivity	Reactivity
Si_2Ca	↘	↗
Si_2Al_2Ca	↘	↗↗
$Si_8Al_6Fe_4Ca$	↗	→
Si_2FeTi	↘	↘
$Si_{2,4}Fe$	↘	↘
Si_2Al_3Fe	→	→

FIGURE 9. Role of the intermetallides in the chloromethylation of silicon

Effect of Heat Treatments

Figure 7 is available only for the cooling rate used, and corresponds to a structure in a non-equilibrium state. For a given analysis, there may be different distributions of intermetallides. The relative proportions of intermetallides found in samples from different locations of a silicon ingot of composition Fe = 0,4, Al = 0,23, Ca = 0,36 per cent are shown in Table III. These results were obtained using an image-processing system coupled with SEM.

As observed variations cannot be explained by the corresponding chemical analysis, we took into account the role of the cooling rate. Five samples containing the same proportion of intermetallides were heat-treated at different temperatures. The relative fractions of the intermetallic compounds for temperatures of heat treatment are shown in Figure 10.

TABLE III
RELATIVE FRACTIONS (%) OF INTERMETALLIC COMPOUNDS IN DIFFERENT PARTS OF AN INGOT

Si_2Al_2Ca	24	27	26	24	28	30
$Si_8Al_6Fe_4Ca$	14	14	14	13	9	6
Si_2Ca	32	33	36	34	36	33
$Si_{2,4}Fe$	29	26	24	29	26	30

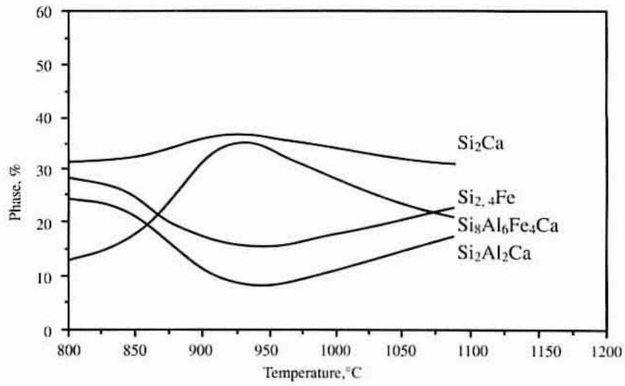

FIGURE 10. Effect of annealing on the relative fractions of intermetallic compounds

How to Produce a Given Structure

From the equilibrium diagram shown in Figure 8 and the results obtained in the experimental trials, we can define the factors governing the structure of industrial silicons.

The trials showed that the precipitation of $Si_{2,4}Fe$, Si_2Al_3Fe, and $Si_8Al_5Fe_7$ easily leads to non-equilibrium conditions. In the case of the ternary Si–Al–Fe phases, the occurrence of incomplete peritectic reactions explains the deviation from equilibrium.

The compositions of the remaining liquid during solidification under non-equilibrium conditions have been calculated. The results show that, for the reasons previously mentioned, we found that the Si_2Al_2Ca phase in silicon had an analysis in the stability field of the phases Si_2Ca–$Si_8Al_6Fe_4Ca$–$Si_{2,4}Fe$. In this case, the effect of slow cooling or of thermal treatment is to bring the system nearer the equilibrium state by lowering the quantities of Si_2Al_2Ca and $Si_{2,4}Fe$, and increasing the Si_2Ca and $Si_8Al_6Fe_4Ca$.

For any other analysis we can define

- the nature of the intermetallides
- how the intermetallides appear during solidification
- the effect of the different cooling rates
- at what temperature the reactions occur between the intermetallides, and therefore the correct temperature for a heat treatment or the necessary temperature for slow or rapid cooling to produce a desired final structure.

Conclusions

These studies gave rise to a better understanding of silicon behaviour and an improvement in quality. Knowledge of the nature and properties of the intermetallides has served to explain the behaviour of metallurgical-grade silicon in many applications, and has shown that the nature and proportion of the intermetallic compounds formed (and therefore the final properties of the silicon) depend on the initial composition of the silicon and on the solidification conditions.

By optimizing these parameters, we can produce the best silicon quality for a final application: the process is better controlled, and the needs of the customer are better satisfied.

Acknowledgments

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