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Carbothermic reduction of silica in a microwave furnace for the production of solar-grade silicon

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العنوان: الإختزال الكربوني للسيليكا في فرن الميكروويف لإنتاج السيليكون من الدرجة الشمسية.

ملخص: تبحث هذه الأطروحة في إنتاج السيليكون الشمسي باستخدام تقنية فرن الميكروويف. يقدم تحليلاً مفصلاً لطرق مختلفة لإنتاج السيليكون من الدرجة الشمسية، وحركية تكوين السيليكون، وتطبيق أفران الميكروويف. ويرد وصف مفصل للتقنيات التجريبية للإعداد والتحليل. توضح النتائج تأثير العوازل على امتصاص الميكروويف، ووضع البوتقة على توزيع الحرارة، وطرق قياس درجة الحرارة في تسخين الميكروويف، وتأثيرات حجم الحبيبات والمواد المصافة على التخفيض الكربوحراري للسيليكا. تقدم الدراسة رؤى مهمة حول طريقة الاختزال الحراري المباشر لإنتاج السيليكون من الدرجة الشمسية باستخدام أفران الميكروويف وتوفر أساسًا للبحث المستقبلي في هذا المجال.

يُظهر البحث أن السيليكون، المطلوب لتصنيع الخلايا الشمسية، يمكن إنتاجه بعدة طرق، مع كون الانخفاض الكربوحراري للسيليكا في أفران القوس الكهربائي هو الأكثر شيوعًا في قطاع السيليكون. تقدم هذه الأطروحة طريقة مبتكرة لتصنيع السيليكون الشمسي باستخدام أفران الميكروويف. تم إنشاء كريات بأحجام مختلفة عن طريق الجمع بين السيليكا والكربون وربطهما بالماء والكحول البولي فينيل. اكتشف التحليل الطيفي لرامان قممًا عند 515 ⁻⁻mm للسيليكون في كريات الكحول البولي فينيل، و 523 ⁻⁻mm، و 794 ⁻⁻m للسيليكون وكربيد السيليكون في كريات الماء. حجم الحبيبات له تأثيرات كبيرة على امتصاص طاقة الميكروويف. أظهر كحول البولي فينيل إمكانية أن يكون رابطًا لإنتاج السيليكون في أفران

الكلمات الرئيسية: فرن الميكرويف؛ الكربون ؛ السيليكا ؛ السيليكون الشمسي ؛ الخلايا الشمسية.

Title: Carbothermic reduction of silica in a microwave furnace for the production of solar-grade silicon.

Abstract: This thesis investigates the production of solar-grade silicon using microwave oven technology. It provides a detailed analysis of various methods for producing solar-grade silicon, the kinetics of silicon formation, and the application of microwave ovens. Detailed descriptions of the experimental setup and analysis techniques are included. The results illustrate the influence of insulators on microwave absorption, crucible positioning on heat distribution, temperature measurement methods in microwave heating, and the effects of pellet size and additives on the carbothermal reduction of silica. The study provides important insights into the direct carbothermal reduction for future research in this area.

The research shows that silicon, which is required for solar cell manufacture, may be produced in a variety of ways, with carbothermic reduction of silica in electric arc furnaces being the most common in the silicon sector. This thesis presents an innovative method to manufacture solar-grade silicon using microwave furnaces. Pellets of various sizes were created by combining silica and carbon and binding them with water and polyvinyl alcohol. Raman spectroscopy detected peaks at 515 cm⁻¹ for silicon in polyvinyl alcohol pellets, 523 cm⁻¹, and 794 cm⁻¹ for silicon and silicon carbide in water pellets. The size of the pellet has significant effects on microwave energy absorption. Polyvinyl alcohol showed potential as a binder for silicon production in microwave furnaces.

Keywords: microwave furnace; carbon; silica; solar grade silicon; solar cells.

Titre : Réduction carbothermique de la silice dans un four à micro-ondes pour la production de silicium de qualité solaire.

Résumé: Cette thèse étudie la production de silicium de qualité solaire en utilisant la technologie des fours à micro-ondes. Il fournit une analyse détaillée de diverses méthodes pour produire du silicium de qualité solaire, la cinétique de la formation de silicium, et l'application des fours à micro-ondes. Des descriptions détaillées de la configuration expérimentale et des techniques d'analyse sont incluses. Les résultats illustrent l'influence des isolateurs sur l'absorption des micro-ondes, le positionnement des creusets sur la distribution de la chaleur, les méthodes de mesure de la température dans le chauffage par micro-ondes et les effets de la taille des granulés et des additifs sur la réduction carbothermique de la silice. L'étude fournit des informations importantes sur la méthode de réduction carbothermique directe pour la production de silicium de qualité solaire à l'aide de fours à micro-ondes et fournit une base pour les recherches futures dans ce domaine.

La recherche montre que le silicium, qui est requis pour la fabrication de cellules solaires, peut être produit de diverses manières, la réduction carbothermique de la silice dans les fours à arc électrique étant la plus courante dans le secteur du silicium. Cette thèse présente une méthode innovante pour fabriquer du silicium de qualité solaire à l'aide de fours à micro-ondes. Des granulés de différentes tailles ont été créés en combinant la silice et le carbone et en les liant avec de l'eau et de l'alcool polyvinylique. La spectroscopie Raman a détecté des pics à 515 cm⁻¹ pour le silicium dans les pastilles d'alcool polyvinylique, 523 cm⁻¹, et 794 cm⁻¹ pour le silicium et le carbure de silicium dans les pastilles d'eau. La taille de la pastille a des effets significatifs sur l'absorption d'énergie par micro-ondes. L'alcool polyvinylique a montré un potentiel comme liant pour la production de silicium dans les fours à micro-ondes.

Mots-clés : four à micro-ondes; carbone; silice; silicium de qualité solaire; cellules solaires.

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" Wise seeds grow and blossom in a rational environment."

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Abbreviation					
DE	Diatomaceous Earth	AC	Activated Carbon		
EAF	Electric Arc Furnace	SoG-Si	Solar-Grade Silicon		
MG-Si	Metallurgical Grade Silicon	Poly-Si	Polycrystalline Silicon		
EG-Si	Electronics Grade Silicon	AC	Alternating Current		
DC	Direct Current	Ppm	Parts Per Million		
Ppb	Parts Per Billion	ISM	Industrial, Scientific, And Medical		
PVA	Polyvinyl Alcohol	CMC	Carboxymethyl Cellulose		
FDTD	Finite Difference Time Domain	FEM	Finite Element Method		
FVM	Finite Volume Method	FIT	Finite Integration Technique		
Q mass	Quadrupole Mass Spectroscopy	wt %	Weight Percent		
MW	Microwave	DDA	Discrete Dipole Approximation		
MD	Molecular Dynamics	ReaxFF	Reactive Force Field		
LO	Longitudinal Optical	SEM	Scanning Electron Microscopy		
TEM	Transmission Electron Microscopy	ТО	Transverse Optical		

List of abbreviation and symbols

Symbols					
SiO ₂	Silicon Dioxide (Silica)	С	Carbon		
CO ₂	Carbon Dioxide	SiC	Silicon Carbide		
SiO	Silicon Monoxide	Si ₃ N ₄	Silicon Nitride		
ZrO ₂	Zirconium Dioxide	AIN	Aluminium Nitride		
AI_2O_3	Aluminium Oxide	BN	Boron Nitride		
Y ₂ O ₃	Yttrium Oxide	Fe3O4	Iron Oxide		
Cr_2O_3	Chromic Oxide	ZrO ₂	Zirconium Dioxide		
CaO	Calcium Oxide, Calcia	CaO	Calcium Oxide, Calcia		
Т	Temperature	Р	Pressure		
t	Time	ΔH	Enthalpy Change		
ΔS	Entropy Change	ΔG	Free Energy Change		
Pco	Pression Partielle CO	P _{SiO}	Pression Partielle SiO		
\vec{D}	Electrical Displacement Density	E	Electric Field Strength		
\vec{E}	Electric Field Vector	E	Effective Field Strength		
E_0	Initial Intensity	\dot{q}_v	Volumetric Heating Energy		
α	Degree Of Attenuation	D_p	Penetration Depth		
T_c	Critical Temperature	P _{abs}	Microwave Power Absorbed		
\vec{P}	Polarization Vector	f	Frequency		
tan δ	Dielectric Loss Tangent	C_p	Heat Capacity		
χ	Susceptibility	el	Electronic		
io	lonic	or	Orientation		
SC	Spatial Charge	ε_0	Permittivity Of The Vacuum		
З	Permittivity	ε_r	Relative Permittivity		
$\mathcal{E}_{r,F}$	Permittivity Of The Fluid	$\mathcal{E}_{r,P}$	Permittivity Of The Particle		
K _x	Equilibrium constant	K _p	Equilibrium constant		

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Introduction

Solar energy is the energy found in sunlight and can be converted into electricity by a photovoltaic cell, which is an electronic device capable of directly converting incident sunlight into electricity, benefiting from the conduction properties under illumination of some semiconductor materials [1].

Photovoltaic panel production is still at an early stage of development, and it is currently very difficult to predict the technical, economic, and social patterns that will be followed by their implementation before reaching maturity. However, if photovoltaic cells are to become the main source of energy in the future, one should ask what materials and natural elements are crucial for ensuring the long-term stability of this energy source. This is particularly important for semiconductor materials whose bandgap must ensure effective conversion of sunlight into electricity. The history of solar cells, dating back to the 1950s, reveals intensive research and development, covering a wide range of disciplines and leading to many innovations.

Diversity of semiconductors in their compositions and structures, such as organic, inorganic, intrinsic, extrinsic, homo-junctions, hetero-junctions, amorphous, and crystalline, is a continuous source of dilemmas that brings new research achievements to the scientific and industrial environment [2]. It may take several years before scientific and industrial companies can solve these challenges and answer the questions raised above.

Currently, silicon is the dominant semiconductor material that converts light into electricity. There are two main classes of silicon: amorphous and crystalline. Crystalline cells are either single or multi-crystalline. Within each group of technology, several variants can be distinguished. The latest market research conducted by commercial consultants, organizations, and government agencies confirms the dominance of silicon-based technologies, in particular crystalline silicon technologies [3].

Many renewable energy ventures are developing solar-grade silicon production to reduce the cost of solar panels, resulting in many developments and potential solutions from companies

and research laboratories around the world. It is still in the phase of growth and testing to achieve the desired results for entering the global market. Examples include JPM Silicon, which develops a potential silicon manufacturing process and sustainable solutions for the production of silicon metal through recycling of silicon waste from solar cell production [4], and HPQ Silicon Capital, which aims to become a High Purity Silicon Metal vertically integrated producer and a Solar Grade Silicon Metal metallurgical producer used in the manufacture of multi- and monocrystalline solar cells [5].

This research was carried out in the first phase of the SSB project, and after the end of the project between Algeria and Japan, it continued to find sustainable and competitive solutions to many traditional methods, aiming to upgrade the important second step in the production cycle of silicon, corresponding to the metallurgical field, which is the carbothermal reduction of silica for solar-grade silicon production.

The purpose of this thesis is to investigate the production of solar-grade silicon using the direct carbothermic reduction method, with a specific focus on the use of microwaves as a heating source. The work is divided into five chapters, each of which covers different aspects of the production process.

Chapter I provides an overview of the general routes of solar-grade silicon production, including the manufacturing of metallurgical-grade silicon, upgrading metallurgical-grade silicon to solar-grade silicon, and the main routes for silicon production.

Chapter II focuses on the kinetics of silicon production and the main factors that affect direct carbothermic reactions, such as temperature, raw materials, gas atmosphere, and catalyst. This chapter also covers heat transfer modes and the objectives and goals of the work.

Chapter III explores the use of microwaves for silicon production, including microwave heating fundamentals, interaction with matter, thermal runaway, materials for use in high-temperature microwave furnaces, and the main microwave furnace component.

Chapter IV describes the experimental setup, including operational procedures, measurement methods, elaboration of materials for the microwave furnace, and techniques for analysis.

Chapter V presents the results and discussion of the experiments, including the effect of insulators on microwave absorption, the effect of crucible location on heat distribution, the effect of temperature measurement methods in microwave heating, and the effect of pellet size and additives on silica carbothermic reduction.

In conclusion, this study provides insights into the direct carbothermic reduction method for solar-grade silicon production, with a focus on the use of microwaves as a heating source. The results of the experiments provide a foundation for future research in this field.

Furthermore, I provide a perspective on the potential and importance of microwave technology not only in developing solutions for manufacturing solar-grade silicon but also in various other industrial applications. As an academic challenge, I also emphasize the importance of passing on this technology to future generations through collaboration between the university community and the industry sector. This transfer will enable an increase in the percentage of academic scientific publishing and allow students to unleash their ideas, enhance their awareness, and ultimately enable them to create successful projects and even startups that contribute to the country's economy.

Chapter I. General routes of the Solar Grade Silicon production

process

The manufacture of photovoltaic cells requires raw materials, and among the most important materials is silicon. This element is the second most available element after oxygen and forms about 28% by weight of the Earth's crust, as shown in Figure 1. However, as a free material in nature, it never occurs because it is strongly combined with oxygen, forming silicates and oxides [6].



Figure 1. Abundance (atom fraction) of the chemical elements in Earth's upper continental crust as a function of atomic number. They are classified into categories: (1) rock-forming elements (major elements in green field and minor elements in light green field); (2) rare earth elements (labelled in blue); (3) major industrial metals (global production > ~3×107 kg/year; labelled in red); (4) precious metals (purple); and (5) the nine rarest "metals"—the six platinum group elements plus Au, Re, and Te (a metalloid) [7].

Silicon (Si), like many other elements, can exist at room temperature in different structures made up of the same atoms, called allotropes of silicon, which are arranged differently.

The first of these is amorphous silicon, which is flexible and not exceptionally strong because the atoms in the structure are mostly connected throughout, but some atoms are not bonded to their maximum capacity. In general, the amorphous phase is a dark brown powder and is a popular material for many applications such as solar panels, calculators, watches powered by solar cells, and more.

Atomic Number	14
Atomic Weight	28.086
Melting Point:	1414°C, 2577.2°F, 1687.15 K
Boiling Point:	3265°C, 5909°F, 3538.15 K
Density (293.15 K):	2.33 g/cm ³
Liquid Density (1687.15 K):	2.57 g⋅cm ³
Specific Heat (298.15 K):	0.168 Cal/g/K
Surface Tension (1687.15 K):	736 mN/m (=dyne/cm)
Heat of Fusion:	39.6 kJ·mol⁻¹
Heat of Vaporization:	383.3 kJ·mol⁻¹
Heat of Atomization:	451.29 kJ·mol ⁻¹
Thermal Conductivity (298.2 K):	1.49 W/cm/K
Thermal Expansion (298.15 K):	2.6 μm·m⁻¹·K⁻¹
Molar Heat Capacity:	19.789 J·mol ⁻¹ ·K ⁻¹
Mohs Hardness:	7

Table 1. Typical properties of silicon.

The second one is crystalline silicon, which is stronger and more stable than amorphous silicon, due to the atoms in the structure being completely bonded. It is also called polycrystalline and has a metallic luster and a greyish colour. Like amorphous silicon, it is used in solar cells and also in electronics microchips, computers, smartphones, and any other electronic device.

To manufacture solar-grade silicon, various processes are needed to purify and transform it into photovoltaic cells, but the silicon purity depends on the method of extraction [8]. In this chapter, we will discuss the different production processes for this material. Finally, we will conclude with the main objectives of this work.

I.1 Manufacture of metallurgical grade silicon

I.1.1 Silica reduction methods

Since the source of silicon is quartz or silica, there are many studies on the mining process to reduce silica (SiO₂) in various applications. For example, preparing alumina particle-reinforced aluminium-silicon composite using the aluminothermic reduction of silica method [9]. This approach is similar to the calciothermal reduction method proposed in a good project by researchers who used amorphous silica extracted from rice husk (Figure 29) to extract silicon of acceptable purity through calciothermal reduction [10]. Silica can also be reduced by the magnesiothermic reduction method, using magnesium to produce silicon. This method has been used in a significant project for lithium-ion battery applications and beyond, due to the increasing demand for portable energy applications using silicon as an anode material to increase the capacity of the batteries, particularly the lithium-ion cell [11].

Among all these different methods, this thesis will focus on the study of a new approach to direct solar-grade silicon (SoG-Si-99.9999% pure) production by carbothermic reduction of silica.

I.1.2 The Carbothermic Reduction of Silica

Metallurgical grade silicon (MG-Si), with a typical purity of 97.5 to 99.5% Si, is an important metal used in the industry as an alloying agent in the aluminium industry, a deoxidizer in the steel making industry, and to produce electronic grade silicon (EG-Si 99.9999999999999999999999999) for the electronics industry as well as solar cells. Silicon metal is produced by the carbothermic reduction-smelting process using the traditional method that was used at the beginning of the twentieth century in submerged electric arc furnaces, as shown in Figure 2.

At that time, the furnaces were developed for ferrosilicon and other alloys. However, manufacturers' interest over the past decades in developing production according to market supply and demand prompted them to use larger furnaces and improve material use more efficiently and process control to reduce costs and increase the quality levels of its final products.



Figure 2. Schematic illustration showing a submerged electric arc furnace (EAF) with a standard silicone production process [12].

In this process, raw materials such as quartz and carbon (such as coke, charcoal, and/or woodchips) are selected to achieve high product quality for the production of silicon. Within the reaction zones, the reduction of quartz by carbon occurs at temperatures between 1300 and 2000°C and at atmospheric pressure.

Depending on the size of the furnace, the manufacturing process requires a large amount of energy, demanding 10-30 MWh/ton of produced silicon, as well as higher temperatures of up to 2000°C between the electrodes in the lower part of the furnace.



Figure 3. General view of the electrical process path to the reaction zone (Viridi.iQ GbmH).

The electrical energy path is shown in Figure 3, which is brought into the reaction zone by means of three large graphite electrodes submerged in raw materials. This process requires a large input of electrical energy to activate the arc necessary for the expected chemical reactions. The arc furnaces are supplied by two different types of electrical current. One of them uses 3-phase AC electricity with 3 columns of electrodes, and the other uses DC electricity with only one column of electrodes. The energy sources used vary in operating costs according to the factory's policy.



Figure 4. Typical raw materials and MG-Si process manufacturing pathway (Viridi.iQ GbmH).

Quartz, carbon, and wood chips are added from silos at the top of the furnace. As the materials are transported through the furnace, oxygen is removed from the quartz, and liquid silicon is tapped from the bottom of the furnace at higher temperatures into ladles. Small amounts of aluminium and calcium are added and refined through this process. After the refining process, the liquid silicon is cast into beds to solidify. The solidified silicon is then crushed and sieved as shown in Figure 4 to supply the customers.

The synthetic metallurgical-grade silicon component is not appropriate for use in photovoltaics and electronics, depending on the source raw materials of silica, carbon, and the form of electrodes. Furthermore, boron and phosphorus dopant impurities are far too high in concentration (> 50-100 ppmw) to allow sufficient compensation procedures [13].



Figure 5. Overview of the electrode change after consumption (Aero Industries Inc).

Electrode technology is an important aspect of the industry's current development: half a dozen types of electrodes ranging from pre-baked to self-baking electrodes are in use or in the development process. The electrodes will be gradually consumed and replaced by new electrode elements screwed to the top of the arc furnace of the electrode system, as shown in Figure 5.

I.2 Upgrading Metallurgical Grade Silicon to Solar Grade Silicon

Solar grade silicon (SoG-Si), or polycrystalline silicon (Poly-Si) better known in the electronics sector (EG-Si), is obtained through the purification of metallurgical silicon and will be used to

make ingots of silicon. In general, there are different processes that can be classified into two main families for the production of solar grade silicon: chemical/metallurgical and electrochemical routes. The chemical route currently dominates almost the entire market, with two major processes using trichlorosilane (75%) and monosilane (25%).

Trichlorosilane and monosilane are the two dominant chemical processes used in the production of solar-grade silicon. The chemical route is preferred due to its ability to produce a material of higher purity, which is essential for the electronics industry. However, the chemical route is associated with high energy consumption and poses a risk due to the use of chlorinated products. On the other hand, the electrochemical route involves the dissolution of quartz in fluoride and the three-layer electro-refining of silicon, which is less energy-intensive and less hazardous. Despite this, the electrochemical route is not widely used in the industry due to its lower efficiency and higher production costs.

Element	Concentration (ppm)	Element	Concentration (ppm)
Aluminium	1000-4350	Manganese	50-120
Boron	40-60	Molybdenum	< 20
Calcium	245-500	Nickel	10-105
Chromium	50-200	Phosphorus	20-50
Copper	15-45	Titanium	140-300
Iron	1550-6500	Vanadium	50-250
Magnesium	10-50	Zirconium	20

Table 2. Typical impurity concentrations found in metallurgical-grade silicon (MG-Si) [14].

A list of selected SoG-Si production and refining methods is presented in Table 4, and the following subsections will explain some examples from the section in more detail. The demand for and use of silicon depends mainly on the severity of its purity, as shown in Tables 2 and 3, on the typical impurity concentrations of both metallic and electronic silicon, respectively.

Element	Concentration (ppb)	Element	Concentration (ppb)
Arsenic	< 0.001	Gold	< 0.00001
Antimony	< 0.001	Iron	0.1-1.0
Boron	≤ 0.1	Nickel	0.1-0.5
Carbon	100-1000	Oxygen	100-400
Chromium	< 0.01	Phosphorus	≤ 0.3
Cobalt	0.001	Silver	0.001
Copper	0.1	Zinc	< 0.1

Table 3. Typica	l impurity	concentrations	found in electr	onic-grade s	ilicon (EG-Si) [14].
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I.3 The Main Routes for Silicon Production

The Siemens process and the Metallurgical route are the two most important process chains for purifying silicon from metallurgical grade silicon (MG-Si):

I.3.1 Chemical route of Siemens process

The Siemens process is a chemical route used for the production of polycrystalline silicon. It involves the synthesis of silicon-containing gaseous compounds, primarily chlorosilanes such as trichlorosilane, monosilane, and tetrachlorosilane [15]. These compounds are purified through distillation and then subjected to thermal decomposition to deposit polycrystalline silicon.

However, this process generates a significant amount of chlorinated waste, making it necessary to operate in sites with large industrial capacities and adhere to strict regulatory requirements, such as the Seveno sites in the European Union. To address these environmental concerns, various recycling methods can be employed, which involve the recycling of chlorinated chemicals, hydrogen, and heat. These measures aim to mitigate the environmental impact and improve the sustainability of the Siemens process.



Figure 6. a) Scheme of the core of the Siemens process. A gaseous precursor is introduced into the reactor and coming into contact with the heated silicon rods dissociates into silicon (REC, Graphic: Bernreuter Research), b) Example of real reactors.

As shown in Figure 7, the Siemens process operates in three phases and produces a gaseous release of $SiHCl_3$ trichlorosilane. Its yield is 25%, with an energy consumption of about 150 KWh EF / kg. It is the method that has traditionally been used by the electronics industry.



Figure 7. The phases of operation of the Siemens process.

I.3.2 Other chemical processes

In the modified cycle of Siemens, the deposition is carried out continuously in a fluidized bed reactor as shown in Figure 8. The silicon grains are formed on precursor silicon particles suspended at 600-800 ° C in a mixture of silane / hydrogen gas, and are recovered at the reactor bottom. The latter alternative has the advantage of providing reduced energy

consumption and time for deposition. This method, initially unique to monosilane, was extended to silicon deposits based on trichlorosilane.



Figure 8. a) Simple fluidized bed reactor schematic, b) Silicon granular material [16].

As shown in Table 4, there are other chemical purification processes using chlorine that differ in certain variations [17]. In all cases, the first step is to separate the Si from metallic impurities by reacting the crushed MG-Si with chlorine gas (Cl₂) or hydrogen chloride (HCl). Chlorosilanes of the SiHCl₃ or SiCl₄ type are formed from this interaction, and chloro-metallic complexes such as FeCl₃, AlCl₃, and BCl₃ are easy to extract.

The following steps allow the production of pure Si from chlorinated silanes through distillation, ion exchange into molten salts, or pyrolysis, depending on the process. The silane path, the second most widespread, uses triple distillation of trichlorosilane to synthesize monosilane (SiH₄), which is then used to deposit the silicon through thermal decomposition. Other examples include the Wacker, Sundermayer, Chisso Corp., or Bayer processes.

Companies currently working on the silicon deposition reactor, which is the last stage of the process, are looking to change the conventional chemical route to adapt the product to meet demand. This is the case for companies such as Wacker, REC Silicon, MEMC, Solar Grade Silicon, and Hemlock, which are turning to fluidized bed technology to replace the Siemens reactor. Certain types of reactors, including the Joint Solar Silicon Free Space Reactor and the Tokuyama Revised Filament Reactor, are also being tested.

I.3.3 Metallurgical route of Elkem process

The whole challenge of the metallurgical route is to reduce production costs while at the same time ensuring sufficient quality for solar applications. Several manufacturers and research institutes are currently developing processes to eliminate the passage of gaseous compounds with the aim of saving energy. Metallurgical methods generally consist of a sequence of successive melting and solidification allowing the gradual removal of impurities, based on the case, different methods may be used.

Among other examples, the European project SolSilc brought together research laboratories and industrialists from Sweden, Norway and the Netherlands to improve the process of carbothermal reduction from very clean materials (high-purity quartz and carbon): this time, solar silicon is obtained directly from quartz.



Figure 9. Acid leaching of silicon in Elkem Solar Process, the impurities are removed by acid leaching and the remained solid is silicon (www.elkem.com).

The most advanced company is Elkem Solar (Norway), which has developed a process that is currently under industrialization [18] as shown in Figure 9. It consists of the treatment of metallurgical silicon with calcium silicate slag at high temperature followed by chemical leaching at low temperature [19]. Residual impurities are collected on top of the ingot obtained after direct solidification. The blocks removed will then be reintroduced upstream into the cycle.

The first studies show that the quality of the obtained solar silicon is similar to that of the polycrystalline silicon marketed on the traditional Siemens route [20]. Cell efficiency is also

within the specifications, approximately 15-16% [21]. The energy consumption for large-scale processing would be about 25-30 kWh/kg of initial material, or 20% of the Siemens process expenditure [22].

I.3.4 Other Metallurgical processes

The PhotoSil project as shown in Figure 10, led by the French company Apollon Solar [23], brings together the expertise of CEA-Liten, CNRS and FerroPem.



Figure 10. Schematic direction of the PhotoSil process for upgrading metallurgical grade silicon (UGM-Si) to solar grade silicon (SoG-Si), which passes from the Conventional Process and FerroPem, compared to the Siemens process path.

The method consists of the first fusion solidification, which enables the segregation of metallic impurities that are much less soluble in the solid than in the liquid; the remaining impurities (in particular boron) are then extracted by the treatment of the liquid with reactive plasma

resulting in the formation of volatile compounds [24]. Development was validated at the beginning of 2008 on batches of more than 50 kg, and at the end of 2008 cell yields were measured at 15%. Other companies are engaged in the metallurgical approach: Kawasaki Steel, Dow Corning ... etc.

Other ways of producing solar silicon still exist in production, as shown in table 4, and research is progressing in electron beam melting [25], leaching after aluminothermic reduction, electro-transport in a magnetic field, electrochemical process, and so on. Also, some projects, such as silicon nitride dissociation in a solar furnace [26] or the use of rice straw as a source of silica [10], are being investigated.

I.4 Direct reduction as an alternate route for the production of solar grade silicon

Direct reduction is considered an energy-saving alternative to the production of SoG-Si, which is one of the alternative methods of carbothermal direct reduction of silica, from a single process of reduction with high-temperature treatment for the production of solar grade silicon as shown in Figure.11.

Among the first companies to use the direct method of reduction is the American company Dow Corning, which laid the foundation stone in 1979 for the principle of direct reduction of carbothermic to solar grade silicon [44]. In those years, it was the only one to follow a new approach to the production of solar grade silicon due to the small market for solar cells and lack of competition in the industrial sector at that time.

Among the first companies to use the direct method of reduction is the American company Dow Corning, which laid the foundation stone in 1979 for the principle of direct reduction of carbothermic to solar grade silicon [44]. In those years, it was the only one to follow a new approach to the production of solar grade silicon due to the small market for solar cells and lack of competition in the industrial sector at that time.



Figure 11. Schematic path comparison of: a) The Siemens silicon process with more than solar purity by means of metallurgical grade silicon. b) Direct reduction process path from raw materials to solar grade silicon.

However, in recent years, numerous projects for the direct extraction of SoG-Si have started due to the inability to produce the silicon needed for solar cells in sufficient quantities, causing the market price of silicon to rise to more than \$475/kg [45].

Nevertheless, market prices have improved by declining over the last decade due to the rapid expansion of production capacity throughout the entire value chain, bringing the price of solar silicone to less than \$12.5/kg [46]. Despite the development of promising methods of direct reduction, it has not been able to keep pace with the quality and purity of silicon produced through the traditional chemical pathway, and due to the high cost of production, many ongoing projects for direct reduction have been discontinued.

Process Route	Raw material	w material Chemical Reactions / Temperature / Pressure				
	Chemical/Metallurgical Approach					
Trichlorosilane based [28]	Metallurgical grade silicon	Si(s) + 3 HCl(g) → HSiCl ₃ (g); (1000°C). 2 HSiCl ₃ (g) + H ₂ (g) → Si(s) + SiCl ₄ (g) + HCl(g)	Hemlock HSC, Siemens, Wacker, Tokuuyama, etc			
Monosilane based [29]	Metallurgical grade silicon	3SiCl ₄ (g) + 2H ₂ (g) + Si(s) → 4SiHCl ₃ (g); (500°C, 30 MPa, catalyst). 4SiHCl ₃ →3SiCl ₄ + SiH ₄ ; (60°C, 0.3 MPa). SiH ₄ (g) → Si(s) + 2H ₂ (g); (800 – 850°C).	REC, MEMC, Joint Solar silicon GmbH			
Fluoride processes [30]	By-products of phosphoric acids and phosphoric fertilizers	H_2SiF_6 (I) + 2NaF(s) → Na ₂ SiF ₆ (s)+ 2HF(I) Na ₂ SiF ₆ (s) → SiF ₄ (g) + 2NaF(s); (650°C) SiF ₄ (g) + 4Na (I) → Si (s) + 4NaF(s); (500°C)	Wacker-chemie and Dow croning			
Zincothermic reduction [31]	Silicon halide, pure Zinc	3SiCl ₄ (g) + 2Zn (l, g) = 2ZnCl ₂ (g) + Si (s); (800°C, 1 atm)	Umicore, Shientsu, Chisso etc			
Aluminothermic reduction [32]	Silicon halide, Pure Aluminium	3SiCl ₄ (g) + 4Al (l) = 4AlCl ₃ (g) + 3Si (s); (400 - 1200 [°] C, 1 atm)	Shinetsu Chemicals, Sumitomo Chemicals etc			
Reduction by Alkali/alkaline earth metals [33]	Silicon halide, Pure Sodium	SiCl ₄ (g) + 4Na/K (g) = 4NaCl/KCl (l) + Si (s); (800 - 880 $^{\circ}$ C, 1 atm). SiCl ₄ (g) + 4Na (l, g) = 4NaCl (g) + Si (l); (1727 – 1927 $^{\circ}$ C, 1 atm).				
Reduction By Hydrogen [34]	Silicon halide , Hydrogen	SiCl ₄ (g) + 2H ₂ (g) = 4HCl (g) + Si(l); (>1412 [°] C)	City Solar AG Corporation etc.			
Hallidothermic reduction [35]	Silicon halide, Aluminium subchloride	SiCl ₄ (g) + AlCl _x (g) → Si (l) + AlCl ₃ (g); (1000°C, 1 atm)				

Table 4. Selected processes for the production and refining of SoG polycrystalline silicon [27].

Table 4. (Continued)

Carbothermic reduction [36]	Ultrapure quartz, carbon black. Oil black, gas black	SiO ₂ (s) + 2C(s) = Si(I) + 2CO(g); (>1900 [°] C, 1 atm)	SOLSILC and SPURT, Dow Corning, Elkem, Siemens, Kawasaki, Heliosil, etc.
Gas phase reduction of Pure SiO ₂ [37]	Quartz, Carbon black, Hydrogen	$SiO_{2}(s) + C(s) \rightarrow Si(I) + CO_{2}(g); (1300-1500^{\circ}C), (10^{-3}-1 \text{ torr})$ SiO_{2}(s) + Si(I) → SiO(g) SiO(g) + H_{2}(g) → Si(I) + H_{2}O(g); (1700 - 1900^{\circ}C, 1)	
Electrochemical Approach			
Three layer Electro refining [38]	Metallurgical grade silicon	Me (Na, K, Ca, Ba, etc) \rightarrow Me ⁿ⁺ + ne ⁻ ; (1700K) (Anode) Si ⁴⁺ + 4e ⁻ \rightarrow Si(I); (Cathode)	NTNU, SINTEF
Direct electrolytic reduction of SiO ₂ [39]	Pure silica	$SiO_2(s) + 4e^- \rightarrow Si(s) + 2O^{2-}(1123K)$	
	ļ	Refinement Methods of MG-Si	
Refinement of MG- Si: Etching/Acid leaching [40]	Metallurgical grade silicon	Crushing \rightarrow Sieving \rightarrow Acid Leaching (HCl, HF, HNO ₃) with Stirring (mechanical or ultrasonic) at 50°C for 8 hrs \rightarrow Washing & Drying	Hemlock, Elkem ASA, Heliotronic, etc
Refinement of MG- Si : Slag process [41]	Metallurgical grade silicon	$[B] + (3/2) O^{2^{-}} + (3/4) O_{2} \rightarrow (BO_{3}^{3^{-}}); 1500^{\circ}C$ $[P] + (3/2) O^{2^{-}} + (3/4) O_{2} \rightarrow (PO4^{3^{-}})$	Nippon Steel, Crystal Systems, etc
Refinement of MG- Si : electron beam and Plasma [42]	Metallurgical grade silicon	Electron beam melting (Phosphorus removal) \rightarrow Plasma(Ar-O ₂ , Ar-H ₂ O etc) treatment(Boron removal); (2027°C) \rightarrow Directional solidification	JFE, Univ. Tokyo, Kawasaki steel Corporation, UNICAMP
Refinement of MG- Si : Solidification from Si-Al alloy [43]	Metallurgical grade silicon	Directional solidification of Si - Al alloy to remove Boron (1273-1473K)	Univ. Tokyo
After all, we take a look at previous direct reduction projects in which the purity of silicon achieved after reduction and the content of boron and phosphorus are being compared in Table 5. As complete analyses are not available for all projects, only aluminium, iron, and titanium impurities, as well as boron and phosphorus impurities, are taken into account.

Table 5. Overview of past and current projects for direct reduction (based on [47]).

Project / company	Raw materials	Silicon purity	Boron [ppmw]	Phosphor [ppmw]
Projects from the 1970s				
Dow Corning [44] / Elkem-Exxon	Quartz, carbon black / activated carbon	99,986% ≙ 3N	10,2	4,8
Siemens [15]	Quartz, Carbon Black	99,967% ≙ 3N	1	< 12
Kawasaki Steel [48]	High Purity Silica, Carbon Black	99,989% ≙ 3N	< 0,5	< 0,5
Projects from the 2000s				
FESIL Sunergy	Quartz, Carbon Black	N.A.	0,5	0,4
Real Green Material Technology	Quartz, Carbon Black	N.A.	≤ 0,4	≤ 0,3
N.E.D. Silicon	Quartz, Carbon Black	> 99%	0,7	0,9
SQT / AUZSOLAR / SSRG	Quartz, Carbon Black	> 99,99% ≙ 4N	N.A.	N.A.
Projects with renewable raw materials from the 2000s				
Mayaterials	Rice husk ash, Carbon Black	99,998% ≙ 4N	< 0,001	0,01
RSI Silicon	Sodium carbonate, carbon black, sugar	N.A.	0,2	0,1

Based on the classic production of silicon in an arc furnace, and in the absence of a viable economic solution, none of the above projects are actively pursued in the present market environment. Nevertheless, several innovations and competitive projects for the production of solar grade silicon have emerged with the goal of achieving a low-cost operation.

Although the arc furnace has long been the leading technology in the production of silicon, new ventures have emerged with the development of new furnaces that vary from one another in terms of technology and heat source.

Among the ventures, a project that relies on induction as a heating source [49], and the HPQ Silicon project, which created a new concept combining an arc furnace with plasma treatment, called a plasma submerged arc [50], as well as other projects, JPM Silicon relies on microwave technology as a heat source for the recycling and processing of solar grade silicon [51].

In the following parts, a few examples from the section on the operation and classification of industrial furnaces will be addressed on the basis of various adopted specifications, such as the cooling system and safety issues related to the failure of such systems in the silicon production process and associated equipment.

I.5 Overview and special features of the furnaces

The field of furnace use is vast in industry and there is no single systematic framework for classification. However, they can be categorized in a variety of ways based on their function, temperature range, heat source, energy source, shape, and method of use. The following classification systems will be simplified below conceptually:

• Temperature range

Industrial heating techniques involve a wide range of temperatures, depending in part on the raw material being treated, in part on the cause of the heating operation, and in part on the sub-phase of the manufacturing process. Depending on this, Figure 12 shows the different temperature ranges applicable in metallurgy with examples. The silicon production process

belongs to a very high temperature range and requires a temperature of more than 1650°C, which is higher than the melting point of silicon.



Figure 12. Different temperatures ranges for metallurgy with examples [52]

Furthermore, temperature ranges can be estimated by a colour temperature chart during experiments or by means of devices called temperature sensors, which are instruments used to measure the temperature of a medium. They are classified into two types: contact sensors and non-contact sensors. There are three types of sensors on the market: thermocouples, resistance temperature detectors, and thermometers. In addition, several other temperature sensors are available for use, and one of the best for high-temperature measurement is a highly sensitive 2-color infrared thermometer with a temperature range from 500 °C to 3500 °C [53].

Heat source

Furnaces generate heat to raise temperature either by the chemical energy of the fuel or by the electrical energy that is converted to heat. For example, combustion models of furnaces (carbon-fired) are relatively common, but electric furnaces are preferred when fuel costs are not comparable to other benefits of electric furnaces, such as a wider temperature range [52].



Figure 13. Furnaces classification based on the heat source.

Figure 13 shows the basic method of generating heat in furnaces, which is generally classified into two types: fuel-fired (combustion type) [54], and electric furnaces, which are based on the way electricity is converted into heat energy [54]. The microwave furnace is the main focus in the scope of the PhD thesis, highlighted in blue.

Cooling systems

Various cooling systems are used to operate furnaces in a wide range of industries, particularly in metallurgy and the silicon industry, which require significant quantities of thermal energy. Cooling systems protect furnaces from the high temperatures produced, which play a key role in control and safety operations. There are two types of cooling systems that use either water or air, and monitoring is required for either of these systems to minimize any associated risks.

Cooling water systems may have some operational problems in any application, and water leakage is the most common. The risk of such leakage is that it may interfere with substances or electronic devices (e.g. the motherboard of the control system), which can result in undesired effects and/or reduced cooling performance [55].

The simultaneous presence of a very large amount of heat energy and water in the same phase creates a risk of severe explosions or eruptions [56]. This probability is very likely to be realized if there are any malfunctions or weaknesses in the water cooling system that lead to water leakage. One of the major industrial accidents caused by water leakage occurred at the Carbide Industries LCC facility in Louisville, Kentucky, USA, in March 2011 [57]. Moreover, precise information on all accidents and investigation reports is limited to the public, but brief information has been found on local news websites and in the article [56].

• Other Classifications

Among other classifications, there are various ways to deliver the charging material to the furnace within the furnace room or to the crucibles of different sizes inside the furnace. The charging process may be carried out in batches by manual or automated means, so that the loading material is put in the furnace and heated for a fixed period, and then unloaded. Alternatively, there is another important method that relies on a continuous charging process, which means that the materials are supplied while the furnace is being heated.

Chapter II. Silicon production kinetics and main factors affecting direct carbothermic reactions

The carbothermic reduction of silica is a common industrial procedure in an electric arc furnace for the production of silicon and does not differ in the chemical reactions that occur mainly within the crucible filled with silica and carbonaceous materials according to the simplified reaction equation:

$$SiO_2 + 2C = Si_{(I)} + 2CO_{(g)}$$
 II.1

II.1 Reaction in the furnace

To understand the processes taking place in the arc furnace's crucible, we need to divide the interior space inside the crucible into two regions. The first is a very hot region at the bottom near the electric arc, which we will call the inner zone. The second is the outer zone, where the temperature decreases as we move from the depth of the crucible to the top. Figure 14 illustrates these zones. Additionally, due to thermal conductivity and thermal flux, the temperatures on the surface of the furnace are below approximately 1,550 °C [58].



Figure 14. a) Photograph of the electrode spark arc and the crust build-up of the crust around the gas cavity (Elkem report), b) Distribution of condensed phases and components within the arc furnace in tow zones. Liquid silicon in contact with carbon or SiO₂ may react and reduce the productivity of the furnace by impacting the tapping process [60].

As a number of chemical reactions occur inside the furnace under atmospheric pressure in the range of temperatures from 1,200 °C to 2,000 °C, the chemical equation (II.1) cannot produce silicon directly. Since the reaction chain plays an important role in the production process of silicon, various factors, such as the homogeneity and quantity of substances in the mixture, as well as the diverse energy sources, are also affected by the continuous supply of materials while the furnace is being heated.

Therefore, the thermodynamic and chemical reaction conditions on which the industrial production of silicon is based are considered first to avoid any unexpected outcomes in carbothermic reduction experiments. The direct reduction of silicon in the arc furnace is described as an alternative method for the production of solar-grade silicon, with the aim of raising some questions to find alternative solutions to reduce production costs. Based on the technical questions alluded to at the end of this chapter, the scientific objectives of the related work on direct reduction in the microwave furnace will be determined, and some possible solutions will be illustrated and clarified.

II.2 Thermodynamic considerations of silicon production

Compounds of substances formed in nature cannot be fully described with pure consideration of thermodynamic equilibrium, or even a description of silicon production is not sufficient, due to the complex reaction kinetics [61]. However, thermodynamic consideration allows a multitude of conclusions to be drawn on the basic mechanisms. By considering the thermodynamic equilibrium, the necessary reaction temperatures can be limited more precisely. Using Gibbs' phase rule:

$$F = C - P + 2 \qquad \qquad \text{II.2}$$

The number of degrees of freedom F is defined as the maximum number of intensive variables to determine the state of the system, which can be determined from the number of components C and the number of phases P, plus 2 (refers to the degrees of freedom associated with temperature and pressure of all phases). The different systems can thus be described by the thermodynamic state variables such as pressure P, temperature T, or percent composition. Within the temperature range defined by Paull [62], four condensed phases were thought to exist: SiC, SiO₂, C, and Si, as well as a gas phase composed of SiO_(g) and CO_(g), the phases become P = 6 and C = 3 in the system of silicon, carbon, and oxygen. This means that silicon would only form above the invariant point at approx. 2,700 °C and a pressure needs to be reviewed [60].

However, when several chemical reactions occur within the furnace's crucibles, and because carbon and silicon cannot coexist within the temperature range under consideration, six equations were required to define all possible combinations of two condensed phases plus a gas phase, which in turn describe the system:

$$SiO_{2(s,l)} + C_{(s)} = SiO_{(g)} + CO_{(g)}$$
 II.3

$$2SiO_{2(s,l)} + SiC_{(s,l)} = 3SiO_{(g)} + CO_{(g)}$$
II.4

$$SiO_{2(s,l)} + Si_{(s,l)} = 2SiO_{(g)}$$
 II.5

$$SiO_{(g)} + 2C_{(s)} = SiC_{(s)} + CO_{(g)}$$
 II.6

$$SiO_{(g)} + SiC_{(s,l)} = 2Si_{(s)} + CO_{(g)}$$
 II.7

$$SiO_{(g)} + C_{(s)} = Si_{(s,l)} + CO_{(g)}$$
 II.8

The thermodynamic variables in the SiO₂-SiC-C-SiO-Si system are pressure, temperature, and phase composition. When the SiO partial pressure (P_{SiO}) of the individual reaction is plotted as a function of temperature (1400-2200°C) under isobaric conditions with p = 1 atm, the system can only be fully described by temperature, as shown in Figure 14, and the basic calculation can be found in appendix A.

The gas phase is assumed to consist only of SiO and CO gas for the Si-O-C system during condensed SiO₂-C, SiO₂-SiC, SiO₂-Si, C-SiC and SiC-Si phases with a total pressure of 1 atm. Thermodynamically, reaction (II.4) requires a temperature greater than 1400°C and a low SiO pressure. As a result, a low SiO pressure results in a high response rate, because the reaction rate is determined by the distance from equilibrium.



Figure 15. Partial pressure of $SiO_{(g)}$ in equilibrium with SiO_2 , SiC and C at a total pressure of 1 atm [60].

The equilibrium system of Si-O-C shown in Figure 15 provides a lot of information about the reduction path of silicon dioxide. In general, the path to silicon is SiO_{2(s)}-SiO_(g)-SiC_(s)-Si_(l,s). All three reactions (II.3), (II.4), and (II.5) produce only gaseous products. Each of these reactions divides the area in Figure 14 [63]. The gas is unstable in gas compositions corresponding to the points to the left of them. A composition or temperature with such an order results in gas condensation or a reversed reaction. Reaction (II.6) consumes the produced silicon monoxide gas over a wide temperature range. To be converted to pure silicon, the stable silicon carbide must be heated above 1,811°C.

The Si-O-C system is defined by two invariant points. Silicon carbide is formed in the SiO₂-C-SiC system at 1,512°C as a result of combining reactions (II.3) and (II.6). The following reaction is highly endothermic [64], as one would expect from a reduction reaction involving a highly stable oxide material:

$$SiO_{2(s,l)} + 3C_{(s)} = SiC_{(g)} + 2CO_{(g)}$$
 II.9

and the formation of silicon at 1,811°C as a result of combining reactions (II.4) in the SiO₂-SiC-Si system (II.7)

$$3SiO_2 + 2SiC = Si + 4SiO + 2CO$$
 II.10

The SiO generating reactions in Figure 14's inner reaction zone is highly endothermic; the reaction enthalpy for reaction (II.4) is $\Delta H_{1500^{\circ}C} = 1416.3$ KJ, and for reaction (II.5) it is $\Delta H_{1500^{\circ}C} = 625.0$ KJ. The majority of the heat generated by electricity was consumed by these reactions. They are thought to be the slowest of the proposed reactions and are not limited by chemical equilibrium [60].

The extraction of silicon requires a temperature of at least 1,811°C. Under isothermal conditions, the silicon yield is only 20%. This can be increased to 33% by recovering the rising silicon monoxide with carbon, but it deviates significantly from the current industry yields of over 90%. A closer examination of the reaction mechanism and the course of the reactions far from thermodynamic equilibrium provides an explanation here [60].

II.3 Reaction mechanism of silicon production

As illustrated in Figure 14, the outer zone with temperatures below around 1,550°C on the surface of the furnace [58] and the inner zone with temperatures of at least 1,811°C are to be considered. Temperatures of nearly 2,000°C are assumed on average, with temperatures reaching up to 3,000°C at the electrode spark arc [65]. Individual zones can be given specific functions and reactions.

In the outer zone, silicon is recovered via the reaction of gaseous silicon monoxide of the two previously described reactions (II.5) and (II.6):

$$SiO_{2(s,l)} + Si_{(s,l)} = 2SiO_{(g)}$$
$$SiO_{(g)} + 2C_{(s)} = SiC_{(s)} + CO_{(g)}$$

According to reaction (II.5), the reverse reaction is also referred to as a condensation reaction, which is not synonymous with a condensation reaction in the sense of a phase change.

To what extent the condensation reaction must be regarded as the primary silicon formation reaction is still unknown [66]. The reaction with carbon allows for the further recovery of silicon monoxide and is dependent on the physical properties of the carbon reductant being used, which are one of the determining factors in the achievable silicon yield, so test methods for the so-called SiO reactivity were developed [60].

The SiO reactivity of a carbon is a measure of its reactivity with silicon monoxide. In the test procedure [67, 68] developed by the Norwegian research institute SINTEF, silicon monoxide is generated and passed through a defined carbon sample. The reactivity is measured using the R10 value in [ml SiO], which corresponds to the amount of silicon monoxide that the sample can pass through unhindered during the test.

Furthermore, unabsorbed silicon monoxide is ultimately a value for the reactivity of carbon. However, the amount of silicon monoxide is not measured, but carbon monoxide is detected in the exhaust gas flow. In addition to silicon carbide, this is formed by the reaction of carbon with silicon monoxide, as shown in reaction (II.6):

$$SiO_{(g)} + 2C_{(s)} = SiC_{(s)} + CO_{(g)}$$

The concentration of CO gas initially rises to 18% as a result of the direct reaction of the sample surface before decreasing further during the reaction.

The R10 value represents the amount of unreacted silicon monoxide in ml that can pass through the sample during the calculated period between the CO gas concentration dropping from 18% to 10%. A low R10 value indicates that there is less unreacted SiO gas. As a result, the carbon material's reactivity is increased and it is more capable of reacting with silicon monoxide gas.

In general, the graph in Figure 16 can be used to classify the reactivity of carbons. The graphs show the carbons that are currently used primarily for the extraction of silicon metal in electric arc furnaces.



Figure 16. The measured SiO reactivity ranges of various carbon reductants (20°C, 1 atm), more The R10 value low, means the carbon material can capture and reduce the SiO loss [69].

The development of the SiO reactivity test [70] is significant because it provides information on how to discriminate between different types of chars and cokes, as well as their effectiveness in filtering SiO gas and CO gas through the porous carbon structure, which is directly related to Si yield.

Finally, a phase analysis is used to determine the amount of free carbon and silicon carbide present during the test [71]. The carbon sample with the highest possible conversion is more capable of reacting with the SiO gas formed in the furnace's high temperature zone, indicating that it is acceptable for use in an electric arc furnace. However, there are often inconsistencies between test results and subsequent industrial application.

In addition to silicon monoxide, the necessary silicon is produced in the inner zone (Figure 14). Silicon monoxide is formed via the reaction between silicon and quartz (II.5) or by the reaction between silicon carbide and quartz:

$$2SiO_2 + SiC = 3SiO + CO$$
 II.11

However, the reactions listed here are not pure solid-state reactions; rather, they represent the general equations for the solid-gas-phase processes that are occurring. Based on the Boudouard equilibrium [60], the description using CO-CO2 makes sense and is experimentally plausible:

$$CO_2 + C = 2CO$$
 II.12

As a result, equation reaction (II.5) is written as the outcome of two reactions:

$$2SiO_2 + 2CO = 2SiO + 2CO_2$$
 II.13

$$2CO_2 + SiC = SiO + 3CO \qquad \qquad II.14$$

The actual silicon formation reaction is now carried out in accordance with equation reaction (II.7) derived from the reaction of silicon monoxide and silicon carbide:

$$SiO_{(g)} + SiC_{(s,l)} = 2Si_{(s)} + CO_{(g)}$$

This means that silicon monoxide and silicon carbide are two intermediary products that are required for the production of silicon.

Even if the reaction between silicon carbide and silicon monoxide is considered the primary silicon formation reaction, the effect of the condensation reaction described in (II.5) on the silicon yield can be demonstrated [66]. When the condensate is heated again, it does not convert to silicon monoxide again, but rather silicon separates from the silicon dioxide framework [66]. Further experimental work demonstrates that considering the condensation reaction as the only silicon production reaction is also purely thermodynamically possible [72].

In the industrial process, all of the silicon monoxide emitted must be transformed to silicon carbide using carbon, with an approximately one hundred percent yield possible. The partial pressure diagram in Figure 15 shows that producing silicon at higher temperatures requires a lower partial pressure of silicon monoxide. The dimensionless s-parameter, which represents the relationship between the partial pressure of silicon monoxide P_{SiO} and the atmosphere of silicon monoxide and carbon monoxide, expresses this fact clearly:

$$s = \frac{P_{SiO}}{P_{SiO} + P_{CO}}$$
 II.15

Only at a temperature of 1,980 ° C is s = 0.5, implying that the silicon formation reaction occurs as follows:

$$SiO_2 + SiC = Si + SiO + CO$$
 II.16

This indicates that the free carbon in the furnace's outer zone is sufficient to completely convert silicon monoxide to silicon carbide. This, of course, assumes that it has the necessary SiO reactivity to ensure a sufficient reaction. Figure 17 displays a silicon manufacturing mechanism that can achieve a 100% yield.





As a result, the reactions of silicon extraction can be described as follows:

 Since silicon is produced through solid-gas-phase reactions, the mixture must be sufficiently permeable. Furthermore, a high specific surface area and small particle size are advantageous in this case.

- Silicon extraction is only possible above 1811°C, and complete extraction is only possible at a temperature of 1980°C, according to the known gross reaction equation.
- The SiO reactivity of the carbon used has a significant impact on the yield. Charcoal has the highest SiO reactivity in general as shown in Figure 16.

When using fine-grained materials and, eventually, pellets for direct reduction, the reaction conditions change as the reaction rate increases with decreasing particle size [60].

II.4 Factors affecting silica carbothermal reduction

II.4.1 Temperature

According to studies [73], chemical reactions are influenced by various factors, and carbothermal silica reduction is temperature-sensitive. The change in equilibrium composition of a system starting with 1 mole of SiO₂ and 2 moles of C as the temperature increases at 1 atm can be modelled using HSC software, as shown in Figure 18. Reactions can be noted mainly within two temperature ranges: between 1510°C and 1760°C and over 2220°C. Silica is converted at 1510°C–1660°C into solid SiC and gaseous SiO, and SiC and SiO react further to elemental silicon at a temperature above 2220°C. CO is continuously removed from the reaction zone in a lab or industrial method, and therefore reactions occur under conditions other than those used in equilibrium phase calculations in Figure 18. SiO and SiC release rates are sufficiently low at temperatures ranging from 1200°C to 1400°C [74], and the results show the formation of a significant amount of SiO when the reaction temperature exceeds 1400°C [75].

Furthermore, several studies have found a two-stage reduction process for silicon production, with a higher silicon yield at 2000°C compared to a lower yield at 1950°C [76]. In addition to the control step for reaction rate reduction of SiO_2 to SiO gas by reaction (II.9), it is important to note that the results shown in Figure 18 are not completely dependable since at temperatures above 1100°C, SiO becomes volatile and can be easily vacuum deposited to form amorphous films with small grain sizes [77].



Figure 18. Model by HSC of the composition of the equilibrium system from: 1 SiO₂ and 2 C (moles).

Not to mention the effects of temperature on chemical processes (II.6, II.7, and II.8), the ratios of SiC and Si production, and which chemical reactions will take the longest time in the reaction compared to the others [78]. In the following section, we will look at the properties of raw materials and how they influence the path of chemical reactions.

II.4.2 Raw materials

In terms of the purity of the materials, uniformity in the mixture, and the difference in the ratio between the materials used, the initial powder preparation should be considered as the key component for controlling silicon production.

According to the overall reactions for silicon (II.1) and SiC (II.9) production for total silica conversion, carbon should be in excess for complete silica conversion. Excess carbon stimulates particle contact between SiO_2 and C [79] and increases SiO formation [80].

Due to the effects of silica particle size, milling duration, and the rate of carbothermal reduction, these are critical parameters defining the size and morphology of SiC particles produced [81]. Carbon sources have a significant impact on the morphology of SiC products and the rate of reaction [82], with SiC crystallites resembling carbon crystallites prior to grain development. Finer carbon crystallites react faster than larger ones.

In silicon production, the behaviour of various components depends on many factors such as, the type of raw materials, the temperature in the furnace, the volatility of the elements and their compounds, relative stability of the elements and their compounds and the solubility of the elements in the liquid silicon.

II.4.3 Gas atmosphere

Earlier research has demonstrated that the gas atmosphere can influence the reaction mechanisms and kinetics of several carbothermal reduction processes [83, 84]. For example, the carbothermal reduction of MnO data revealed that MnO is reduced significantly faster in helium than in argon [85]. Similar results were found when MnO, manganese ore, and ferromanganese slag were reduced [86].

The difference between helium and argon was linked to differences in gaseous reactant and product diffusion coefficients, which are substantially higher in helium than in argon [87]. When carbothermal reduction occurs in hydrogen, oxides are reduced to suboxides, and methane is formed as an intermediate reductant.

However, there has been lesser study of the effect of gas atmosphere on the carbothermic reduction of silica. The production of SiC stops when the CO partial pressure (II.9) arrives at the equilibrium value. For subsequent reactions to occur, CO has to diffuse from the reactant mixture.

II.4.4 Catalyst

Several studies have confirmed that in SiC formation, certain transition metals operate as catalysts [81, 88–90]. The addition of the catalyst allows SiC to grow at lower temperatures and increases the carbothermal reduction reaction rate. For example, Fe and Co improve SiO formation without reactant aggregation, allowing SiC production to proceed to near completion with high SiC yield. In SiO formation and agglomeration (or sintering) of the reactants, Mn, Cu, and Ni have a favourable impact. Al and B addition impacts the growth rate of crystal and the predominant crystal structure.

The reaction between SiO and CO favours the formation of whiskers at a higher temperature (1600°C or above) [91, 92]. In the gas-gas reaction to whisker creation via the forming mechanism VLS (vapour-fluid-solid), transition metals (particularly Fe, Co, Ni) have been demonstrated to serve as catalysts [91].

At first, as the temperature increases to the melting temperature of the transition metal, the catalyst is in contact with the substrate. Si and C from SiO and CO vapours are absorbed until super saturation by the liquid globule. SiC nucleation occurs at the substrate contact and continuous gas-species solution into the liquid catalyst pellet enables the whiskers to grow when additional SiC precipitates.

In addition to metal catalysts, the catalytic effects of boron compounds on the reaction product have been reported [93]. SiC produced from rice husk treated with boric acid (H₃BO₃) has shown improved crystallinity, yield, and purity. H₃BO₃ was completely miscible with SiO₂, which decomposes during heating into a liquid phase of HBO₂ and B₂O₃. The fluid phase aided in the migration of SiO₂ particles to the rice husk, increasing the contact between SiO₂ and C and allowing for a better response [94].

II.5 Heat transfer

Heat transfer is a branch of thermodynamics that describes the transfer of thermal energy, and it is one of the most important factors influencing direct carbothermic reactions. The physical laws that describe heat transport between two systems at different temperatures are included in the field of heat transfer.

The transport always occurs from the higher to the lower temperature level. The transported thermal energy is a process variable known as heat in thermodynamics [95]. Heat can be produced using a variety of energy sources.

The various interconnections between these sources are illustrated in Figure 19, with a primary emphasis on heat energy (thermal energy).



Figure 19. Illustration of thermal energy-related energy sources [96].

If we take a look at the thermal energy illustration, friction is ineffective as a heat source because the absolute amount of energy is small. Electrical energy also generates heat. Joule proposed heat by impedance, i.e., electric current (Joule heat), which is used in a variety of everyday activities. Heat can also be used to generate chemical energy. Heat can eventually be classified as heat of vaporization, aggregation, fusion, solidification, or sublimation in a variety of chemical reactions. These different types of heat are frequently mentioned in thermochemical reactions [97]. For example, progress in the field of solar thermochemical processing was investigated [98].

Different heat sources have been classified as either external or internal heating. It is important to note that infrared radiation, a type of electromagnetic wave heating, is classified as external heating, as shown in Figure 20. By taking into account the main laws of thermodynamics, data on the relationship between heat and the change in internal energy of the system can be provided in many examples [100].

However, data on how heat is transferred cannot be provided. Two physical mechanisms describe how heat transfer changes the internal energy of a system. Contact is one method of transferring heat. This means that heat is transmitted via at least one medium. The energy is transferred between adjoining particles, for example, through lattice vibrations in solids or

molecular collisions in fluids. The second method of heat transfer is radiation, which requires no transfer medium because the energy is transferred via electromagnetic waves. The energy of electromagnetic waves is dissipated as heat in the body through absorption processes [101].



Figure 20. The various heat sources are divided into two types of heating: internal and external. Electromagnetic wave heating includes infrared, microwave, and high frequency radiation [99].

Heat transfer by contact is usually distinguished by the different transport processes of heat conduction and convection. During conduction, heat is transported through one or more substances with the same or different thermal conductivities [102]. In convection, also known as convective heat transfer, heat is transferred between a solid body and a flowing fluid. The ability of a fluid to absorb and dissipate heat is demonstrated in the cooling of electrical equipment and in the design of thermal and fluidic systems [103]. Furthermore, temperature has a considerable influence on the stresses that arise in a material, affecting its longevity and durability [104], since each component has a different resistance to the transfer of heat energy.

II.5.1 Heat transfer modes

In engineering processes, various heat transfer techniques are often used [105]. Heat is transferred via three transmission mechanisms in a thermodynamic system with variable

particle temperatures and thus varying particle kinetic energy. In conclusion, heat transfer is classified into three types, as summarized in table 6, and defined below [106]:

- Conduction is the mode of heat transfer in which atoms or molecules of a substance interact with one another. Internal energy flows from atoms or molecules with a higher energy level to those with a lower energy level as a result of random microscopic movements and vibrations, which continuously cause diffusion and collision processes.
 Conduction takes place in solids, liquids, and gases. Solid electrical insulators interact solely through lattice vibrations; in electrical conductors, electron translational movement also contributes to heat conduction. Heat conduction occurs in the absence of a macroscopic flow of material.
- Convection is the most common mode of heat transfer in liquids and gases; internal energy transport occurs in addition to random molecular diffusive motions by macroscopic material flows (i.e., by mass transport). Forced convection occurs when such a flow is caused by an external influence (for example, a fan, a pump, or the movement of a vehicle). In the case of free convection, the flow is caused by buoyancy caused by temperature-related local density differences. During the boiling or condensation processes, a special type of convection occurs. Temperature differences cause changes in density as well as transitions between the fluid's liquid and gaseous aggregate states.
- Radiation heat transfer is a mode of heat transfer in which energy is transported via electromagnetic waves, without the need for a medium for propagation. When electromagnetic radiation hits a body, it can be either completely absorbed, reflected, or transmitted. When radiation is absorbed, the energy of the electromagnetic wave is dissipated in the body as heat. Heat exchange via electromagnetic waves, like conduction and convection, always occurs from a system with a higher temperature to a system with a lower temperature. In theory, all bodies can emit energy in the form of electromagnetic radiation and exchange radiation with one another.

Table 6. Basis summary of heat transfer modes [107]

Heat transfer				
Conduction	Convection	Radiation		
 In conduction, heat transfer between objects occurs by direct contact. Heat transfer occurs due to the difference in temperature. Heat transfer in conduction is slow. Heat transfer occurs through a hot solid object. It does not follow the law of reflection and refraction 	 In convection, heat transfer occurs within the liquid. Heat transfer occurs due to the difference in density. Heat transfer in convection is faster. Heat transfer occurs through intermediate bodies, for example, heat transfer between air and water. It does not follow the law of reflection and refraction. 	 Heat transfer in radiation occurs by electromagnetic waves without the presence of particles. Heat transfer occurs in all objects with a temperature greater than (0) Kelvin. Heat transfer in radiation is the fastest. Heat transfer occurs through electromagnetic waves. It follows the laws of reflection and refraction. 		

Laws involved in the heat transfer process

Fourier law	Newton's law of cooling	Stefan-Boltzmann law		
$O_{cond} = -k \cdot A_c \frac{dT}{dT}$	$Q_{conv} = h \cdot A_s (T_s - T_f)$	$E_{rad} = \varepsilon \sigma \cdot A_s T^4$		
$\begin{array}{c} T_{1} > T_{2} \\ R_{cont} \\ A_{s} \\ \end{array} \\ \begin{array}{c} T_{1} > T_{2} \\ R_{cont} \\ A_{s} \\ \end{array} \\ \begin{array}{c} T_{1} > T_{2} \\ R_{cont} \\ R_{s} \\ \end{array} \\ \begin{array}{c} T_{1} > T_{2} \\ R_{s} \\ \end{array} \\ \begin{array}{c} T_{1} > T_{2} \\ R_{s} \\ \end{array} \\ \begin{array}{c} T_{1} > T_{2} \\ R_{s} \\ R_{s} \\ \end{array} \\ \begin{array}{c} T_{1} > T_{2} \\ R_{s} \\ R_{s} \\ \end{array} \\ \begin{array}{c} T_{1} > T_{2} \\ R_{s} \\ R_{s} \\ \end{array} \\ \begin{array}{c} T_{1} > T_{2} \\ R_{s} \\ R_{s} \\ \end{array} \\ \begin{array}{c} T_{1} > T_{2} \\ R_{s} \\ R_{s} \\ R_{s} \\ \end{array} \\ \begin{array}{c} T_{1} > T_{2} \\ R_{s} \\ R_{s$	$T_{s} > T_{f}$ fluid at T_{f} $Q_{conv} h A_{s} \text{ at } T_{s}$	E_{rad} F_{rad} F_{r		
One dimensional Conduction heat transfer through a stationary	Convection heat transfer from a surface A_s at T_s to a moving fluid at T_f .	If we add the surrounding area with temperature T_{∞} the relationship becomes:		
medium.		$Q_{rad} = h_{rad} \cdot A_s (T_s - T_\infty)$		
(L = dx)		$h_{rad} = \varepsilon \sigma (T_s^2 + T_\infty^2)(T_s - T_\infty)$		

Table 6. (Continued)

Basics of thermal resistance $R_t = \frac{\Delta T}{Q}$			
$R_{t,cond} = \frac{L}{KA_s}$	$R_{t,conv} = \frac{1}{hA_s}$	$R_{t,rad} = \frac{1}{h_{rad}A_s}$	
To decrease <i>R_{t,cond}</i> :	To decrease $R_{t,conv}$:	To decrease $R_{t,rad}$:	
 Increase the cross section of the object, Decrease the length of the object, or Select material with a higher thermal conductivity. 	 Increase the surface area of the object, For the natural convection, consider the configuration so that the temperature difference is increased, or For the forced convection, increase the air velocity 	 Increase the surface area of the object, or select material with a high emissivity 	

Engineers frequently use thermal resistance (i.e. thermal resistance against heat conduction) to calculate heat transfer through materials because there is an analogy between heat diffusion and electrical charge diffusion. Thermal resistance is equal to thermal conductance multiplied by the reciprocal. A thermal resistance may be related to heat conduction in the same way that an electrical resistance is related to electricity conduction. Resistance network models are frequently used as research tools by computational materials scientists [108].

II.5.2 Heat transfer in granular materials

Heat transfer through particle contact and granular material is a combination of conduction, convection, and radiation heat transfer, and it is influenced by particle shape and a number of particle-level mechanisms:

- Conduction within the material,
- Conduction (grain_grain) through the contact area,
- Conduction (grain_fluid/gas_grain) which is essential in partially saturated precipitates
- Radiation at inter grain contacts,

- Conduction through pore fluid,
- Convection in pore fluid,
- Radiation from the particle surface into the surrounding medium.



Figure 21. Standard heat transfer mechanisms paths in materials: ① particle conduction, ② contact conduction, ③ particle/fluid/particle conduction, ④ particle/particle radiation, ⑤ particle/fluid conduction, ⑥ pore fluid conduction, ⑦ pore fluid convection, and ⑧ radiation into the

surrounding medium [109].

Figure 21 describes the heat transfer mechanisms for a spherical grain standard unit in schematic form. Heat transfer could be considered conductive in naturally occurring porous precipitates, particularly fine sands and clays at low temperatures, due to the negligible relative contribution of free convective and radiative mechanisms [110].



Figure 22. proposed SiC synthesis reaction mechanism [78].

The grain dimensions, on the other hand, have an effect on the thickness of the reaction zone, as reported in Figure 22, by "Weimer et al." an adaptation of the shrinking core model for the carbothermal reduction synthesis of beta silicon carbide [78]:

$$K = \frac{1 - (1 - X)^{1/3}}{t} = \frac{k_0}{d} \exp(-\frac{E}{RT})$$

where K = the reaction rate (s⁻¹), k_0 = rate parameter (m/s), E = activation energy (kJ/mole), d = carbon crystallite diameter (m), t = time (s), R = gas law constant (8.314 J/mol.K) and X = silica (or oxygen) conversion.

II.6 Objectives and goals of the work

The aims of this work address the technical-scientific concerns raised in the introduction. The following goals are derived based on the state of the art in science and technology:

- Develop a suitable experimental setup to investigate the reaction temperatures in the reaction mixture of silicon production in the microwave furnace.
- Prepare high-purity raw materials in the form of pellets for testing in the microwave oven. Examine and evaluate the effect of pellet size and additive on the carbothermal reduction yield of silica. Determine the efficiency and reliability of using a microwave device for the silicon carbothermal reduction process.
- Investigate the effect of crucible location on heat distribution in microwave heating experiments. Evaluate the accuracy of temperature measurement in microwave heating and explore alternative measurement methods.
- Develop and test suitable crucibles and insulation techniques for thermal analysis.
 Explore the use of numerical modelling to better understand the formation of specific phases and colours in silicon.
- Determine the necessary conditions, material selection, and protection methods for the safe and effective use of microwave technology in metallurgical research and industrial processes.

In summary, the thesis aims to investigate the potential of the developed microwave process as a viable alternative to silicon production for solar cells and to provide opportunities for academic projects in the industrial development sector.

Chapter III. Use of microwaves for silicon production

The novel approach converts highly pure raw materials into silicone, unlike previous concepts which aimed to reduce solar silicon directly. However, instead of the electric arc furnace, microwaves are used for the first time to produce silicon.

The material is almost immediately heated when quartz and carbon mixtures are irradiated with microwaves. This is mainly due to the excellent microwave absorption property of carbon contained in the mixture. This property is essential for the efficient use of microwaves in silicon production.

The development of a suitable microwave furnace is discussed, starting with the principle of microwave heating. A suitable reaction chamber is then provided in such a furnace with a new conception of the material. This new approach combines theoretical and a series of tactile tests so that fundamental concepts can be examined. In particular, the lack of literature data on material properties for use in microwave furnaces and high temperatures requires experimental tests.

III.1 Microwave heating fundamentals for silicon production

Microwaves are electromagnetic waves with frequencies ranging from 1 to 300 GHz [111], and the frequencies used in industry, science, and medicine today are controlled by ISM bands (Industrial, Scientific, and Medical, ISM) [112]. The microwave heating frequencies of 915 MHz, 2.455 GHz, and 5.8 GHz may be traced back not only to the legislative regulation of the ISM bands but also to technical and economic boundary requirements, so these frequencies have become the industry standard for microwave heating [113].

Today, the most common microwave heating frequency in homes and industries is 2.455 GHz. The microwave source, the magnetron, emits a wavelength of 12.24 cm, which is in the order of magnitude of the items to be heated, improving energy transmission and therefore heating. Because the magnetron is also an electromechanical component, its frequency is affected by its geometry, among other things. Although it is technically possible to produce alternate geometries and hence supply other frequencies, this comes at a high expense, and such a technique is usually not cost-effective. The microwave furnace utilized in this work has a frequency of 2.455 GHz as well.

Microwave heating is the macroscopic heating effect caused by the interaction of a substance with an electromagnetic field as a result of polarization processes. The polarizable particles follow the high-frequency alternating field. The movement of the particles as a result of polarization eventually leads to dissipation and heating of the substance. There is a contrast between the following types of polarization [114]:

- Electron polarization: the polarization of the negatively charged electron shell against the positively charged nucleus.
- Ion polarization: the displacement of ions in an ion lattice, such as quartz.
- Orientation polarization: displacement of polar molecules, such as water.
- Spatial charge polarization: displacement of free charge carriers, such as carbon.

As previously stated, interactions of a substance with an electromagnetic field result in polarization effects, which can be quantified using the electrical displacement density \vec{D} [115, 116]. The following applies to the electrical displacement density \vec{D} of an electrical field \vec{E} in a vacuum:

$$\vec{D} = \varepsilon_0 \cdot \vec{E}$$
 III.1

The permittivity of the vacuum is expressed by ε_0 . The permittivity is a measure of the interaction of a substance with the electric field. The polarization effects described above are taken into account by the polarization vector \vec{P} :

$$\vec{P} = \varepsilon_0 \cdot \chi \cdot \vec{E}$$
 III.2

The following applies to the displacement density in a dielectric:

$$\vec{D} = \varepsilon \cdot \vec{E} = \varepsilon_0 \cdot \vec{E} + \vec{P}$$
 III.3

The microwave fields can be described using phasors when considering a narrow-band steady state. The substance-dependent susceptibility χ is a measure of the polarizability of a substance. The susceptibility is the sum of the individual polarization mechanisms:

Where the subscript el, io, or and sc refer to electronic, ionic, orientation and spatial charge polarization mechanisms, respectively. The susceptibility is related to the permittivity as follows:

$$\varepsilon = (1 + \chi) \cdot \varepsilon_0 \tag{III.5}$$

The permittivity of a substance is always expressed as a multiple of the permittivity of the vacuum ε_0 and as a relative permittivity ε_r :

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$$
 III.6

The dielectric constant is a term used interchangeably with permittivity. Dielectrics are nonconductive materials that permit the propagation of an electric field through them. Their dielectric properties, which are determined by the dielectric constant or coefficient, can be described. However, because the dielectric constant is not a fixed value and can only be specified for dielectrics, the term is being gradually replaced by permittivity.

Since the polarization effects described above are lossy, the permittivity becomes complex:

$$\varepsilon_r = \varepsilon_r' - i \cdot \varepsilon_r''$$
 III.7

The real part of the permittivity ε'_r denotes a substance's polarizability. The imaginary part ε''_r , also known as the loss factor, corresponds to the part of the microwave field dissipated in heat.

The loss part can also be expressed in terms of the loss angle $tan \delta$:

The dielectric constant, also known as the relative permittivity (ε'_r), measures a material's ability to store energy when subjected to an external electric field, such as microwaves. In addition, the dielectric loss factor (ε''_r) indicates the material's capacity to dissipate absorbed microwave energy, converting it into heat. The higher the dissipation capacity of a sample, the less microwaves can penetrate it.

For most dielectric materials, the value of $tan \delta$ is below 0.32. In such cases, the real part of the relative permittivity (ε'_r) is equivalent to the real permittivity (ε_r), with a maximum error of 5% [117].

$$\varepsilon_r' \approx \varepsilon_r$$
 III.9

In addition to the polarization effects, conduction losses (ohmic losses) as the quotient of the specific conductivity σ and the angular frequency ω also contribute to the heating of a material. As a result, the material data obtained through measurements always correspond to an effective loss factor $\varepsilon_{eff}^{\prime\prime}$, which has two components: dielectric and ohmic loss:

As is well known, the energy absorbed per unit volume, also known as power density in the material and microwave power absorbed (P_{abs}) or volumetric heating energy \dot{q}_v in W/m^3 caused by microwaves can eventually be calculated in a simplified manner using the frequency f, the loss factor, and the effective field strength |E|, where σ is the total effective conductivity [118]:

$$\dot{q}_{v} = \sigma |E|^{2} = 2\pi f \varepsilon_{0} \varepsilon_{r}' tan \,\delta \cdot |E|^{2} = 2\pi f \varepsilon_{0} \varepsilon_{r,eff}'' \cdot |E|^{2} \qquad \text{III.11}$$

The loss factor is a key parameter that characterizes the dielectric properties of materials, which determines their ability to interact with electromagnetic fields, such as those produced by microwaves. The loss factor is defined as the ratio of the imaginary part to the real part of the complex permittivity of a material, and it is commonly represented by the symbol $tan \delta$.

In the case of mixed powders, the loss factor is an important parameter that affects their heating performance in microwave processing applications, and corresponds to different variables, including:

- Loss factor vs. frequency: The loss factor of a mixed powder depends on the frequency
 of the applied microwave field. At low frequencies, the loss factor is usually small
 because the polarization mechanisms that contribute to energy dissipation are slow or
 limited. As the frequency increases, the loss factor typically increases as well, due to
 the increasing contribution of faster polarization mechanisms that respond to the
 microwave field. However, at very high frequencies, the loss factor may start to
 decrease due to the onset of waveguide and cavity effects that reduce the interaction
 of the microwaves with the powder particles.
- Loss factor vs. composition: The loss factor of a mixed powder also depends on its composition, specifically the type and amount of constituents that make up the powder. For example, powders containing water or polar solvents tend to have higher loss factors than those containing only nonpolar materials, because the polar molecules can easily align and rotate in response to the microwave field. Similarly, powders containing conductive materials, such as metals or carbon, can exhibit high loss factors due to the generation of eddy currents that dissipate energy as heat.
- Heating rate vs. loss factor: The loss factor of a mixed powder has a direct impact on its heating performance in microwave processing. Generally, powders with higher loss factors heat up faster than those with lower loss factors, because they can absorb more microwave energy and convert it into heat. However, there is a threshold beyond which further increases in the loss factor do not necessarily lead to faster heating, because the powder may become saturated or may start to exhibit nonuniform heating due to hot spots or thermal runaway effects. Therefore, the optimal loss factor for a given powder composition and processing condition depends on a balance between heating efficiency and safety.

- Particle size and shape: The size and shape of the powder particles can influence the interaction of the microwaves with the material, affecting the loss factor and heating performance. Smaller particles and irregular shapes can lead to higher loss factors due to increased surface area and enhanced polarization mechanisms.
- Moisture content: The moisture content of the powder can also affect the loss factor and heating performance. Wet powders tend to have higher loss factors due to the presence of water molecules, which can polarize and absorb microwave energy.
- Density and packing: The density and packing of the powder can also affect the loss factor and heating performance. Denser powders and those with tighter packing can have higher loss factors due to increased inter-particle interactions and reduced penetration of the microwaves.
- Processing time and power: The processing time and power used in microwave processing can also affect the loss factor and heating performance of mixed powders.
 Longer processing times and higher power levels can lead to increased heating efficiency but may also increase the risk of non-uniform heating and thermal runaway effects.

Therefore, when designing and optimizing microwave processing of mixed powders, it is essential to consider all these variables and find the optimal balance between heating efficiency, quality, and safety.

Dielectrics, as weakly or non-conductive materials, can be classified as microwave-transparent or absorbent based on their dielectric loss properties [119]:

- Microwave absorbers, such as water or substances with pronounced dipoles ($tan \ \delta > 0, 1$).

- Transparent materials such as quartz glass or Teflon (tan $\delta < 0,1$).

Metals and other electrically conductive substances must be distinguished from this.

Table 7 compares the microwave properties of the condensed phases in the reaction system to water, which is an example of a very good microwave absorber, and Teflon, which is an example of a microwave transparent substance.

Table 7. Selected materials and their material properties in microwave processes. The values are for a frequency of 2.455 GHz and a temperature of 20°C.

Material	Permittivity $arepsilon_r'$	Loss factor ε_r''	Loss angle $tan \delta$
Teflon (PTFE) [120]	2,1	6x10 ⁻⁴	2,857 x10 ⁻⁴
Fused silica [121]	3,8	3,8x10 ⁻³	0,1 x10 ⁻³
Charcoal [122]	4,2	0,156	3,7 x10 ⁻²
Coal [123]	2,9	0,1657	5,6 x10 ⁻²
Quartz [124]	3,1	0,215	7,01 x10 ⁻²
Water [125]	80,4	9,8892	0,123
Silicon [126]	10	1,5	0,15
Carbon black [127]	130	52	0,4
Silicon carbide [128]	10,5	11,0	1,048

Material properties can vary greatly depending on production processes, grain sizes, surface properties, and so on. Therefore, the use of material data recorded in the literature [129] is usually limited to an initial qualitative evaluation of the respective questions. Only by measuring the samples can more precise statements be made [130]. However, measuring the properties at high temperatures [131] poses a challenge, and suitable measurement methods are still the subject of current research projects [132]. The handling of substance data for mixtures, such as for the reaction system of silicon extraction consisting of quartz and coal, is more complex.

There are some analytical expressions (mixture rules) that can be used to predict the dielectric properties of a multiphase material, and it appears that the mixture properties will be

intermediate between the two components. However, this is not always the case, especially when conductive materials are involved.

For a mixture of quartz and coal, a sufficiently precise value for the dielectric properties can be calculated by means of a mixture rule, which can be used for the design and optimization of a microwave furnace [133]. The effective, relative permittivity $\varepsilon_{r,eff}^{\prime\prime}$ of a quartz-coal mixture can be calculated using the Lichtenecker approximation [134, 135]:

Wich $\varepsilon_{r,F}$ representing the permittivity of the fluid and $\varepsilon_{r,P}$ the permittivity of the particle. Table 8 compares the measured dielectric properties to the results obtained using the Lichtenecker approximation. One disadvantage of the Lichtenecker mixing rule is that it was developed by fitting empirical data. Apart from a theoretical justification involving an artificial decomposition of geometrical shapes of inclusions [136], it lacks a physical model.

A study investigated the criteria for applying mixing rules to the discrete dipole approximation (DDA) method, using elements of different components with varying volume fractions. The study examined several materials, including ice, amorphous carbon, graphite, silicon carbide, silicate, and iron, using mixing rules such as Hanay, Maxwell-Garnett, Lichtenecker, Bruggeman, and Looyenga, in addition to porous materials [137]. However, N. Maron and O. Maron concluded that the best results were obtained using the Lichtenecker mixing rule, but only for a specific volume fraction of inclusions. As a result, they justified the use of the chosen mixing rules based on numerical experiments.

In Table 8, it is evident that the quartz-charcoal mixture utilized for silicon extraction exhibits exceptional characteristics as a microwave absorber. This mixture efficiently absorbs microwaves and can be heated effectively due to the carbon's excellent absorbing properties when subjected to microwaves [138]. The permittivity of the mixture is 2.92, indicating its ability to store electrical energy. With a loss factor of 0.313, the mixture efficiently converts absorbed microwave energy into heat. Furthermore, the loss tangent of 0.108 signifies a high

level of energy dissipation and heat generation when exposed to microwaves. These remarkable properties make the quartz-charcoal mixture highly suitable for silicon extraction purposes.

Table 8. Dielectric property measurements of quartz, charcoal, and a mixture using the stoichiometric reaction equation for silicon extraction and the Lichtenecker approximation for mixing [133].

Material	Permittivity $oldsymbol{arepsilon}_r'$	Loss factor $arepsilon_r''$	Loss tangent $tan\delta$
Quartz	2,67	0,039	0,015
Charcoal	3,24	0,503	0,156
Quartz-Charcoal	2,92	0,313	0,108
Lichtenecker approximation	3,31	0,407	0,123
Quartz-silicon carbide	5,70	0,630	0,111
Lichtenecker approximation	5,85	0,701	0,120

III.2 Microwave interaction with matter

In terms of their microwave behavior, materials can be classified as reflective, transparent, or absorbent. Most of the time, all three effects are present, but one of the properties is always dominant. As a result, three types of substances are frequently formed:

- reflectents: microwaves are reflected in their entirety and cannot penetrate into the material. They are the so-called conductors.
- Transparent: microwaves pass through the entire material without any energy loss.
- Absorbents: microwaves are absorbed by the material, the amount of absorption being dependent on the value of the dielectric loss factor possessed by that material.

Depending on the nature of the material, a portion of the microwave radiation is always directed at the surface when the material interacts with the microwave field. The microwave field's electric field strength decreases as the other part of the microwave radiation penetrates

the material. This attenuation depending on the path x can be approximately described by an exponential function [139]:

The penetration depth, or the distance into the sample where microwave radiation is attenuated to 1/e (=36.8%) of its initial intensity (E_0), is determined by how strongly the material interacts with the electromagnetic wave, and is defined by the degree of attenuation α as [140]:

At a sufficient small loss angle, the penetration depth can be calculated in a simplified manner to [141]:

$$D_p = \frac{\lambda}{4\pi} \cdot \left[\frac{2}{\varepsilon'_r \cdot \left(\sqrt{1 + (\varepsilon''_r / \varepsilon'_r)^2 - 1} \right)} \right]^{\frac{1}{2}}$$
 III.14

According to [113], Eq (III.14) can be simplified if: $\varepsilon_r'' \leq \varepsilon_r'$, the loss angle will be $tan \delta \leq 1$. Since this condition is fulfilled for most dielectric materials, the penetration depth is approximately described with:

$$D_p \approx \frac{\lambda}{2\pi \sqrt{\varepsilon'_r \cdot \tan \delta}}$$
 III.15

Figure 23, illustrates the mechanism of radiation attenuation, the evolution of electric field strength, and the heating power density during one-sided microwave irradiation of an absorbent material.

The equations (III.14 and III.15) only apply to dielectric materials. Metallic materials, while primarily reflective of microwave radiation, can also be heated with the microwave [143]. However, this is not a case of volumetric heating; rather, heat is generated as a result of induced eddy currents in a thin layer on the surface [144]. However, it should be noted that

the published information can only be regarded as a guideline, as the precise material composition and measurement method are usually not mentioned.



Figure 23. Schematic representation of the occurring heat power density depending on the penetration depth D_p and the sample size x [142].

The penetration depth is an important metric for determining where the heat development is concentrated in the volume of material to be heated. The size and geometry of the material to be heated should be considered [145] when developing the internal temperature profile [146].

However, the material to be heated must be irradiated all around and microwave reflections in the furnace must be considered. This produces a complex microwave field that surrounds the material to be heated but is very inhomogeneously distributed in the absence of any special measures [147]. This is due to the nature of microwave radiation and the shape of the reactor chamber. Nonetheless, the described heating process can result in a simplified adaptation of a microwave heating system [148].

Microwave absorption in materials is controlled by their electromagnetic properties [149] while thermal properties control heating during microwave irradiation [150]. As a result of microwave interactions with materials, materials can be classified into four major groups [151]:
- Transparent: These materials have very high penetration depths of several meters $(D_p \gg x)$, and low loss insulators allow microwaves to pass through without being absorbed, resulting in little energy loss (these materials have a low dielectric loss factor, such as Quartz, Teflon, and Aluminum oxide. As a result, there will be little interaction with the material and the energy of the microwaves is not converted into heat.
- Reflective: These materials are non-loss insulators, with a micrometer penetration depth (D_p << x). They are conductor materials that reflect microwaves with no or negligible energy absorption. As a result, the material's surface is only heated in a very thin layer.
- Absorbent: These materials have a penetration depth roughly equal to the size of the heated body (D_p ≈ x), and high loss (e.g., water, silicon carbide, and charcoal). They are dielectric materials in which microwaves are completely absorbed depending on the value of the dielectric loss factor. The majority of the microwave energy can thus be absorbed and used to heat the body's interior.
- Mixed absorbers: These are advanced materials [152], such as composites or multiphase materials [153], with at least one phase acting as a low loss insulator and the other(s) acting as a high loss insulator. The high dielectric loss factor phase interacts with microwaves and is heated, whereas the other phase is conventionally heated.

The amount of energy reflected, transmitted, and absorbed is determined by the component's material properties and the temperature of the material being irradiated; these materials are known as partial absorbers. According to Equation (III.14), as the frequency and effective dielectric and magnetic loss factors increase, the depth of penetration decreases [154].

According to Table 8, the penetration depth of the mixture (Quartz-Charcoal) is 10.55 cm, as calculated by Equation (III.15). This value corresponds to the depth of penetration only when the two mixed materials meet conditions such as purity, homogeneity of the mixture, and particle size. Therefore, the diameter of the sample under irradiation must not exceed this value for effective heating. If some properties differ, the depth of penetration changes.

One limitation of using microwave energy to process materials is the insufficiency of dielectric data in the microwave frequency range as a function of temperature. In addition to expanding databases on the dielectric properties of materials in relation to temperature, moisture content, and frequency [118], there is a need to develop predictive models that allow for more effective use of this technology in manufacturing.

Even the electromagnetic models used to calculate the microwave field distribution require a significant amount of computation. Therefore, the most reliable way to design a microwave or hybrid heating process is to conduct an experimental study of the material's microwave absorption. This applies not only to the material being heated but also to furnace components in the microwave field.

The interaction of the microwave with the material is greatly influenced by several factors, as explained earlier. However, the most important factor among these is the effect of the mixture's homogeneity (e.g., carbon and silica) on the depth of penetration, whether the components are solid or unfused, and whether the raw materials are fine-grained or granular. Nonetheless, the edges and corners of the grains or pellets partially increase the field strength [155], leading to improved energy consumption when using granular raw materials or pellets. Consequently, the absorbed microwave energy is slightly higher than that of a comparable solid.

Moreover, the significance of inventions in the development of powder material processing using microwaves and their extended applications in the field of high temperature was challenged and successfully patented, for example [156].

III.3 Thermal runaway

Thermal runaway is the rapid, continuous, and uncontrolled rise in temperature, usually in the interior of a sample. It is caused by heating substances with strong temperature dependence on their dielectric properties, which are influenced by the temperature distribution. This uncontrolled overheating can potentially destroy materials or components [157], or a region

of the sample, and can take several hours to occur. The microwave absorption timescale is determined by the size of the piece, the specific heat, the local value of thermal conductivity, and the maximum possible microwave power delivered to a sample. Some substances, for example, have very high microwave transparency at room temperature, while their microwave absorption increases with temperature. Ceramic materials such as alumina [158] and zirconia [159] are examples of such substances.

The imaginary part of the loss factor ε_r'' has a strong temperature dependence on many dielectric substances, increasing exponentially with temperature, and significantly affects the heating of a substance in the microwave field. This increased microwave absorption can lead to a further temperature rise in the material, which increases microwave absorption even more. Typically, this increase is gradual until a critical temperature T_c is reached, at which point an exponential increase in ε_r'' is observed. Figure 24 represents this response qualitatively. The rise of ε_r'' with *T* is much less pronounced in some materials, making it more difficult to determine T_c .



Figure 24. Qualitative progression of the loss factor versus temperature [118].

Overheating spots can occur when the material being heated is inhomogeneous and contains additives or foreign particles with higher microwave absorption. One of the important reasons for this is the inhomogeneity of the microwave field, where the location with the maximum energy of the standing wave is warmer than the surrounding environment. Another reason is that the material has very good thermal insulation properties, but its shape is not suitable for the depth of penetration, concentrating heat in a specific place inside the material. Local melting can occur within the material if the microwave power is not sufficiently reduced after the critical temperature is locally raised. Thermal runaway is a particularly dangerous phenomenon in microwave heating, especially for the thermal insulation materials used in the furnace. The destruction of the internal thermal insulation layer is invisible from the outside, difficult to predict, and ultimately results in costly furnace repairs.

There has been a lot of interest in theoretical explanations for the thermal runaway phenomenon [160]. However, it is difficult to determine who was the first to attempt to describe thermal runaway. Nevertheless, the research of Roussy et al. is certainly significant [161], and the thesis of Dr. Wu Xiaofeng provides a thorough explanation of their research [162].

III.4 Materials for use in high temperature microwave furnaces

High-temperature applications require materials with unique properties, primarily for lining high-temperature furnaces. These materials must be insulating, durable, and possess low thermal conductivity. Additionally, they need to have high thermal shock resistance and a high melting point. Materials meeting these requirements are generally referred to as refractory materials.

Refractory materials used in microwave furnaces must also exhibit suitable dielectric properties. This is crucial to protect the crucible that holds the carbon-silica reaction mixture and shields the silicon from any contaminants that may penetrate from the furnace materials. This becomes particularly important at the furnace's edge, especially in larger furnaces, where the reaction mixture either does not react or reacts only to a small extent [163].

The use of lightweight refractory bricks, typically made of oxides or silicates, is only feasible at low temperatures and under non-reducing conditions. Industrial ceramics are further classified into oxide and non-oxide ceramics, including silicate ceramics. However, piezo ceramics do not play a significant role in the specific application under consideration [164]. Table 9 provides an overview of the ceramics considered in the context of this discussion.

Natural ceramics	Synthetic / technical ceramics			
Silicate ceramics	Oxide ceramics	Non-oxide ceramics		
Clay Pottery	Alumina	Nitrides	Carbides	
Porcelain	Aluminum Titanate	• Aluminum Nitride	Borcaride	
• Mullite	Hafnium Oxide	• Boron Nitride	Silicon Carbide	
Cordierite	 Magnesium Oxide 	 Silicon Nitride 	•	
•	• Silica / Quartz	•		
	• Titanium Dioxide			
	• Yttrium Oxide			
	•			

Table 9. Industrial ceramics classification in general [164]

Many oxide materials are transparent to microwave energy between 0.915 GHz and 2.45 GHz. However, oxides with impurities that increase their electrical conductivity, such as mobile ions or mobile defects, can couple to electromagnetic radiation in this frequency range, with most of the heating being electronic.



Figure 25. tan δ for various crucible considered: (SiC, 3.02 GHz); (mullite 3GHz); (ZrO2, 2.45 GHz); (AIN, 8.5 GHz); (AI2O3, 3.7 GHz); (BN, 4.9 GHz); (Y2O3, 5 GHz); (graphite, 2.45 GHz); (Fe3O4, 2.45 GHz) [165].

Figure 25 presents an overview of crucible ceramics [165], but the results are presented with limited data due to the inability to compare all materials across the entire temperature and microwave frequency range. Therefore, these values should be considered typical.

Producing silicon in a microwave furnace requires suitable crucible materials that meet thermal and chemical requirements, in addition to other demands. Electric arc furnaces used in industrial silicon production are typically lined with graphite, silicon carbide, and refractory bricks [60]. Electrographite is mainly used in high-purity arc furnaces, such as those utilized in the direct reduction projects described in Chapter I.4 [44, 65].

In contrast, graphite and silicon carbide are excellent microwave absorbers. Crucibles made of these materials absorb a significant amount of energy in the microwave field, weakening the field. Therefore, it may not be possible to achieve a high-temperature region within the material. Depending on the application and experiment type, the crucible material chosen must also meet thermal conductivity requirements.

Microwave absorption properties are influenced by factors such as particle size [166], dopants [167], density [168], phase [169], and overall geometry [170]. For a suitable crucible or insulation, it is desirable for it to be as microwave-transparent as possible, meaning that the loss factor $tan \delta$ should be minimized to reduce its own microwave absorption.

Excessive internal microwave absorption can lead to heating and potential material failure, while also reducing the available energy for the intended application. Ion polarization is the primary source of heat generation in thermal insulation materials [117], and no thermal insulation material is completely transparent to microwaves. Additionally, microwave absorption often exhibits a strong temperature dependence.

The dielectric data of most materials are either partially known or completely unknown, necessitating their determination to ensure the suitability of a material for use in a microwave furnace. A preliminary selection of eligible materials can be found in the thesis of Dr. Michal Buryan [171].

Various materials commonly used in industrial furnace construction were examined for their microwave properties, particularly their absorption capacity. Chamotte and other lightweight bricks, commonly used in furnace construction, showed relatively high microwave absorption compared to other tested materials. On the other hand, materials such as carbon and carbidic ceramics, as well as compounds like CaO, Cr₂O₃, and ZrO₂, should be avoided due to their high microwave absorption. Vacuum-formed ceramic fiber plates based on SiO₂ and Al₂O₃ exhibited excellent properties. These ceramic fibers, also known as high-temperature wool products, have already been tested in high-temperature microwave furnace experiments [172].

III.5 The main microwave furnace components

The microwave furnace being considered is a multimode microwave resonant cavity [173] with a capacity of 1 kg of silicon per hour. The furnace should provide a maximum power of 24 kW at a rated microwave frequency of 2.45 GHz. Figure 26 shows the basic structure of such a microwave furnace, along with its most important technical components.





Different field configurations are formed depending on the geometry of the main cavity resonator (reactor chamber) of the furnace [174], as well as the parts of this component and the sample loaded with different materials to be heated. Depending on the field configuration, some microwave radiation is reflected back into the waveguide and thus does not contribute

to sample heating. Adaptation networks, in the form of a 3-Stub-Tuner, are thus used to increase the efficiency of the microwave oven [175].

A 3 Stub-Tuner consists of three movable metal rods that can be adjusted to push microwaves back into the reactor chamber based on the return microwave power. This enables reactor chamber efficiencies of more than 90% to be achieved.

The reflected microwaves, which propagate in the waveguide despite the tuner, are thermally dissipated to a water load in a circulator (Ferrite Devices). This allows the calculation of the unused microwave power based on the temperature of the water.

The circulator is primarily used to protect the magnetron from being severely damaged by reflected microwaves [176]. Depending on the intensity of the microwaves, irradiation of the magnetron would lead to a reduction in performance and service life [177].

The microwave power source is set up at one end of the system. When selecting a power source, the following factors must be considered: the necessary power level, cost, method of control, power supply ripple level, and form factor. Once the needs are identified, selecting an adequate power source is usually an easy option. Appendix B contains an overview of the aforementioned devices that can be installed [178].

Chapter IV. Experiment Setup

Microwave heating system trends in the manufacturing industry vary by application. As shown in Figure 24, the microwave furnace system designed in this study will be powered by four magnetrons that, when combined, can create the requisite microwave power of 24 kW. However, Figure 27 illustrates the architecture of these four subsystems, each of which includes a magnetron (①), circulator (②), and automatic tuning system (③), along with four rectangular waveguides that allow microwaves to enter the reactor chamber (④). The microwave power of each subsystem is infinitely adjustable from 0.6 to 6 kW. The temperature on the crucible side will be detected using an infrared digital pyrometer (⑤).



Figure 27. Diagram of multimode microwave furnace components.

IV.1 Operational procedures and measurement methods

The use of four magnetrons instead of one has the advantage of allowing the field distribution in the reactor chamber to be altered by varying the individual magnetron powers [179]. The power output of each magnetron can be infinitely adjusted, allowing different powers to be applied depending on the required operation and providing varying heating speeds of the mixture, with temperature being the only measured variable. The data of the controller and tuner used are transmitted to a PC via an RS232 interface and are used for test documentation. The following variables are recorded:

- 1. Microwave power as a control or control variable.
- 2. Absolute pressure (0 1.3 bar) and target performance of the vacuum pump.
- 3. Actual and regulated volume flow rates of the protective gas (Argon) inside the reactor chamber.
- 4. Measured temperature of the reaction mixture using:
 - Infrared digital pyrometer on the crucible side, or
 - Thermocouple in the sample.
- 5. via the fully automatic tuner:
 - Incoming microwave power from magnetron.
 - Reflected power from the reactor chamber.
 - Position of the metal pins used to minimize reflection.
- 6. At the recoolers system:
 - Cooling water temperature (the maximum allowable water temperature is set to 25°C and is lowered cyclically to 20°C).

The controller can be used for fully automatic program-based system control and regulation [180]. Power, temperature, pressure, and volume flow can all be adjusted or controlled over time [181]. Temperature measurement is the most critical variable in this project because it allows for statements about possible reactions and the energy efficiency of the process [182]. However, pyrometer measurements require knowledge of the emission coefficient of the reaction mixture [183]. Furthermore, because the emissivity coefficients of the mixture's materials change with temperature during the reaction, the pyrometer reference value in the process must be adjusted [184]. It should also be noted that pyrometer measurement results are influenced if the surface properties of the material change due to contamination or decomposition, such as in aluminium, where emissivity depends on the oxide layer structure, which is significantly temperature-sensitive [185]. However, because the emission coefficients

of the individual components and their temperature dependence are mainly unknown, the emission coefficient is estimated to be $\varepsilon = 0.95$ for high temperatures [186].

IV.2 Elaboration material for microwave furnace

IV.2.1 Raw materials

In this section, we will briefly explore which materials are used and how the mix is made for this part. Carbon and silica are well-known and diverse production sources, but a study has demonstrated that they can be extracted from rice husk [187], as illustrated in Figure 28.



Figure 28. Amorphous silica and activated carbon production from rice husk [187].

• Carbon

The carbon used in the process has a specific impact on the process due to the significantly varying reactivities and heating behaviour of different starting materials in the microwave field, which is determined by their different amounts of carbon and volatile components and different structures. The carbon used has an average particle size of 20 µm and is sourced from Kojundo Chemical Lab. Co., Ltd., Japan. For example, graphite, which has the largest carbon concentration (>99%), has only low reactivity due to its crystalline structure [188]. The microwaves induce eddy currents in graphite due to its metallic character, resulting in an increased field and favouring plasma ignition or starting an arc discharge [189, 190]. In

contrast, charcoal has a highly porous structure that provides a large internal surface area for reaction and facilitates the diffusion of the components in the reaction mixture. It also has less ash (2-3%) than coke (up to 10%). As a result, charcoal has high reactivity and is ideally suited for the process, although it is more expensive than other forms of coal.

• Silica

Silica is an important inorganic substance that finds use in a variety of industrial applications such as biomedical applications, molecular sieves, and catalysts. The sources and costs of silica vary depending on the application, and the silica used in our work has an average particle size of 63 µm and is sourced from Kojundo Chemical Lab. Co., Ltd., Japan. It has a purity ratio of 99.9%.



Figure 29. Procedures for manufacturing silica from rice husk [191].

In terms of producing solar-grade silicon, the consensus is to use high-purity silica and reductive agents that are almost free of boron and phosphorus [36]. The demand for purer sources of silica has led to attention being drawn to silica extracted from sources other than geological quartz or quartzite rocks.

In this context, the LMESM lab team at USTO University is working on projects to extract silica from raw diatoms and increase their purity [192]. This work will help to reduce the cost of importing and extracting silica from natural sources such as Algerian desert sand [193, 194], as well as the cost of manufacturing solar-grade silicon. Furthermore, as shown in Figure 29, various approaches are being used to improve the purity of silica extraction from various sources, including rice husk.



Figure 30. Silica system phase diagram [195].

Silica is a mineral that crystallizes in various forms depending on the conditions of pressure and temperature, as illustrated in Figure 30. The forms of silica are known as α -quartz (stable below 573°C), β -quartz (stable from 573 to 870°C), tridymite (stable from 867°C to 1470°C), cristobalite (stable from 1470°C to 1723°C), coesite (stable at pressures of 2-3GPa and from 700 to 1700°C), stishovite (stability field unknown), moganite, and keatite [196]. Silica dust causes silicosis, a progressive long-term lung injury caused by small particles of quartz rock [197]. To avoid risks when working with silica or other chemicals, it is important to follow the safety rules and guidelines of the laboratory.

• Granulation process

The granulation process is the process by which particles of silica and carbon in a mixture adhere together to form pellets, in order to prevent the separation of the mixture's components. The most important thing is to reduce the leakage of SiO gas from the reaction mixture when it is formed and increase its proportion to react with carbon (reaction II.8), which is important in the chemical reaction for silicon formation.

Sample	Mixture [g] SiO₂−C	Binder agent	Pellets size [mm]	Ratio of binder by weight [%]
(a)	200	water	5	10
(b)	200	water	7	10
(c)	200	water	10	10
(d)	200	PVA	5	3

Table 10. Pellets of different sized, with or without binder.

The homogeneity level must be considered when evaluating the quality of pellets that require the mixing of solid particles. When particles vary in size or density, uniform mixing becomes significantly more challenging [198]. Many researchers have used the wet granulation approach [199], which involves the use of a liquid, with or without a binder, in a disc granulator (Appendix C).

For this study, a mortar and pestle were used to mix 3 moles of crystalline silica powder with 2 moles of carbon black (Appendix C). As shown in Table 10, the binder was mixed into the 200g mixture of $3SiO_2$ and 2C at 3% weight for PVA and without binder at 10% weight for pure water. Minor changes in link weight ratios were observed due to the presence of residue in powder agglomerates [200]. The prepared powder was dried and placed in the granulator, and the mixtures were sprayed with pure water while the inclined disc was rotated for around 15 minutes. The granules were dried in the pan at 80°C for 90 minutes after the rotation stopped.

After drying, the pellets were sifted and selected using a sieve with 2-10 mm mesh holes. We selected 5, 7, and 10 mm pellets made of water only and took 5mm pellets made of PVA, as shown in Table 10. We chose one specific size for PVA as a bond material because different sizes were studied, and this size proved to be the best compared to larger sizes when PVA was used.



Figure 31. The steps involved in preparation of pellets using the wet granulation technique.

Figure 31 illustrates the steps required for making pellets using the wet granulation technique. The first phase involves using the standard method of creating granulates from silica and carbon. The mixture is then fed into a mortar and sprayed with a binder (water or PVA). The pestle vigorously mixes the components to ensure that carbon is bonded to silica as the first layer, in a manner similar to the microscale architecture technique [201]. The subsequent steps have already been described.

With this method of preparation, different forms of pellets can be made, and the polymer can be easily changed. Much research has been published on the effect of different polymer compositions on the shape, thermal energy storage capacity, thermal conductivity, seepage resistance characteristics, and mechanical properties of pellets [199, 202]. Based on these references, the general properties of the mixture can be improved to build its compound mix, with the aim of producing solar-grade silicon in a continuously running process.

IV.2.2 Crucible and insulator setup

The requirements for a good insulating material are essentially the same as those for the reaction envelope materials (crucible).



Figure 32. a) Crucible and insulator setup diagram; b) actual shot of the setup.

Before assembling the crucible and insulator as illustrated in Figure 32, the following requirements must be considered when selecting ceramics from the group listed in Table 9:

• Thermal properties:

- High temperature resistant up to 2,000°C
- Very low thermal conductivity (<1.5 W/m-K).
- Low heat capacity (C_p < 800 J/kg-K)
- high application temperatures or sufficient thermal shock resistance if necessary.
- Thermal expansion possibly similar to silicon (2.6 4.7×10^{-6} /K) or possible material combinations.

• Chemical properties:

- Inert to reactions from the reaction system.
- Purity of the material must meet the requirements for solar grade silicon.

• Dielectric properties:

• High microwave transparency (loss angle tan $\delta < 0.01$).

IV.3 Techniques for analysis

The techniques currently used to evaluate powder mixing before and after an experiment differ [208]. In our experience, we used Raman spectroscopy to analyse our products. One simple example of how to distinguish and determine whether a powder is hydrophilic or hydrophobic, as shown in Figure 33, is by using water. These properties have a significant impact on the homogeneity of the mixture.



Figure 33. Water containing both hydrophilic silica (a) and hydrophobic silica (b). When they are mixed with water, the fundamental difference becomes clear: Hydrophilic products can be completely wetted by water, whereas hydrophobic products do not mix at all (AEROSIL® products, EVONIK).

IV.3.1 Raman Spectroscopy

Raman spectroscopy (Appendix D) is a very useful technique for studying the molecular structure and morphology of heterogeneous materials, and it is now considered complementary to infrared spectroscopy. Different materials have different vibrational modes and, thus, different Raman spectra.

Raman spectroscopy is thus a useful technique for material identification. There is an important distinction between Raman spectra obtained from gases and liquids and those obtained from solids (like crystals). For gases and liquids, we refer to the various vibrational energy levels of the individual molecules that comprise the material.

However, crystals are made up of molecules with different vibrational energy levels. As a result, the entire crystal lattice vibrates at the macroscopic level. Phonons are the macroscopic vibrational modes.



Figure 34. Raman scattering and molecular vibrations (JASCO Global).

The Raman effect is based on light scattering, which includes both elastic (Rayleigh) and inelastic (Raman) scattering at different wavelengths caused by molecular vibrations as shown in Figure 34. Rayleigh scattering is a million times more intense than Raman scattering. As a result, to obtain Raman spectra, Rayleigh scattering must be prevented from overwhelming the weaker Raman scattering.

Raman spectra are obtained by exciting a sample with a high-intensity laser beam and passing the scattered light through a spectrometer. The Raman shift is the difference in energy between incident and scattered light. The vertical axis in the resulting spectrum represents the intensity of the scattered light, and the horizontal axis represents the Raman shift wavenumber (cm⁻¹). Further information on the theoretical principles of Raman spectroscopy and its potential use in the life sciences can be found in references [209, 210].

Chapter V. Results and Discussion

This chapter is dedicated to highlighting the outcomes and conclusions of our experiments on the utilization of microwave technology for silicon extraction. It also covers the adjustments made to the experimental materials to enhance the evaluation of these methods, as well as the design and application of a microwave device that greatly improves the efficiency of the silicon carbothermal reduction process.

V.1 Effect of insulators on microwave absorption

The thermal insulation materials required for our experiment, as outlined in the previous chapter, have unique requirements that differ from those commonly advertised for their properties of low and stable thermal conductivity, the required temperature range, adequate mechanical strength, and consistent performance at high temperatures. However, the results reveal that the insulation materials are significantly affected by the gas atmosphere, as depicted in Figure 35.



Figure 35. a) The combustion of Aluminium Silicate Fiber with the integrity of alumina foam bricks, b) The use of alumina foam bricks alone demonstrates that insulators are affected by the external environment rather than the crucible.

Figure 35 illustrates that while alumina is typically a microwave-transparent material, its surface can be affected by external factors. Figure 35(a) shows the combustion of aluminium silicate fiber, but the alumina foam bricks are not affected. Figure 35(b) demonstrates that when using alumina foam as insulators, they are affected by the external environment rather

than the crucible. This is because gases emitted from the crucible adhere to the surface of the insulator, and as they accumulate, they become materials that absorb microwave energy. As a result, the insulator burns along with it, preventing almost all microwave energy from reaching the mixture being heated. Other experiments have also revealed that the insulator can be affected by the external environment when chemicals that produce gases are present [211].



Figure 36. Temperatures on the surface of the crucible sample: a) when use aluminium silicate fiber with alumina foam bricks, b) When use alumina foam bricks alone.

As illustrated in Figure 36, the surface temperature of the crucible was recorded during a microwave heating experiment using two different insulator materials. The temperature did not exceed 1264°C when using an insulator consisting of aluminium silicate fiber and alumina foam bricks. However, when using alumina foam bricks alone as the insulator, the temperature also did not exceed 1267°C, but the reflected power of the microwave energy was not effectively absorbed by the pellets, causing damage to one of the magnetrons. This implies that both insulator materials, influenced by the external environment, effectively prevented the crucible surface temperature from rising by reducing the penetration of microwave energy.

V.2 Effect of crucible location on heat distribution

The use of insulators in a microwave heating experiment resulted in low temperature gradients on the surface of the crucible. This is due to the reduced penetration of microwave energy, which leads to less direct heating of the material.

In order to further study, the distribution of the electromagnetic field, the crucible was also tested without insulators. It is essential to understand the temperature-dependent permittivity to improve thermal distribution and reduce any heterogeneity in the electromagnetic field.



Figure 37. Heat distribution in the crucible in different positions: a) position A, the crucible melted in the bottom, and b) position B, the crucible was cracked all over.

The results depicted in Figure 37 reveal non-uniform distribution of electromagnetic microwave energy within the furnace chamber. Crucible (a) positioned at (A) experienced partial melting, whereas crucible (b) positioned at (B) developed cracks across its surface. These disparities in crucible heating caused temperature fluctuations on their respective surfaces, as illustrated in Figure 38.

Understanding the significance of these temperature fluctuations, as demonstrated in Figure 38, is vital to the study. Further investigation is required to comprehend the underlying physical and chemical processes involved in phase transitions among different states of matter (solid, gas, liquid, or plasma). These fluctuations can be attributed to a combination of factors encountered during the experiment, notably the formation of cracks on the crucible surfaces.



Figure 38. Temperature measurement on the surface of the crucible samples: a) Crucible in position A; b) Crucible in position B.

Cracks in the crucible can have a significant impact on the state changes of the material within the crucible, as well as the temperature of the system. When cracks are present on the surface of the crucible, heat loss can occur through these cracks, leading to a decrease in the system's temperature. Additionally, the presence of cracks can also lead to the clogging of these cracks with deposits of gases and reactions that occur inside the crucible, which can cause an increase in temperature.

Furthermore, the pressure and temperature of a system are closely related to the state changes in the material. As pressure and temperature change, the phase of matter also changes. For example, increasing the temperature or decreasing the pressure can cause a material to change from a solid to a liquid, while decreasing the temperature or increasing the pressure can cause a material to change from a liquid to a solid. However, when there are cracks in the crucible, the external environment may affect the internal temperature and pressure, leading to a change in the phase of matter in the crucible.

Crucible deformation and melting, which can lead to the destruction of the crucible, are major concerns in microwave heating processing. However, the observations of the crucible in position (A) align with simulations using the COMSOL Multiphysics software [212]. This

software simulates the electromagnetic field and thermal distribution inside the crucible during the heating process. The simulation results indicate that during the heating process, there is movement in the hot region, meaning that the hot spot is not fixed in one location. This is due to the majority of the microwave energy being absorbed on the surface of the material at high temperatures, as illustrated in Figure 39. This causes the material's surface to heat up faster than the interior, leading to a dynamic hot region. Therefore, the simulation results provide insight into the behaviour of the crucible during the heating process, helping to understand and mitigate the risk of crucible deformation and melting.





Santos et al. [212] simulated the electromagnetic field pattern during the heating process and found that the distribution of the electric field is not uniform. This non-uniformity causes continuous changes in the hot spots, and the thermal variability does not occur at the same

rate. The observable cracks in the crucible are caused by differences in thermal expansion during cooling when a liner is not used, emphasizing the importance of selecting a crucible that is compatible with the reaction occurring in the pellets to avoid contamination, leakage, or crucible failure that could lead to furnace damage. Furthermore, the position of the crucible can affect the distribution of the electric field, as depicted in Figure 40.



Figure 40. Simulation of the electric field distribution in the reactor chamber for different insulating plate heights and crucible locations [213] (JPM Silicon GmbH).

The material's thermal runaway phenomenon, which results in crucible cracking, poses a significant challenge for microwave engineering. Numerical techniques that simulate the distribution of electric fields can help in understanding the underlying causes of thermal runaway. However, due to the fact that many material properties change with temperature, obtaining accurate measurements are a challenging task [214]. As illustrated in Figure 37, understanding the causes of thermal runaway in a material is critical.

The position of the material in the reactor chamber is crucial in achieving the desired temperature profile necessary for efficient silicon extraction. The temperature profile must have a high-temperature zone located at the bottom of the sample where the material is placed for effective silicon separation. However, creating this temperature profile is a complex task that requires precise control of the reactor chamber's temperature and the positioning of the material. As part of the project funded by the German Federal Foundation (DBU) for the Environment [215], JPM Silicon GmbH developed an alternative investigating solutions to this challenge in collaboration with the Institute of Thermodynamics at the Technical University of Braunschweig and Fricke and Mallah Microwave Technology GmbH.





As shown in Figure 41, a strategy was devised to address the issue posed by ambient gases and maintain the insulator from external influences while regulating the temperature within the crucible. This approach effectively counters the detrimental effects of the surrounding gases and ensures stable thermal conditions within the crucible. In summary, the reason for the gases sticking to the alumina insulation and not the crucible in the experiment is complex and involves various factors, such as surface properties, chemical reactions, temperatures, contaminants, and microwave radiation. Further investigation is required to fully comprehend the difference in gas behaviour between the two surfaces.

One significant consideration is the surface properties, which can affect the ability of gases to adhere to a surface due to physical and chemical characteristics such as roughness, hydrophobicity, and wettability. The alumina insulation may have unique surface properties that make it more susceptible to gas adhesion compared to the crucible surface. Additionally, microwave radiation can also impact the behaviour of gases by altering temperature, pressure, and the distribution of electric charges on surfaces, influencing the behaviour of gases and their adhesion to surfaces.

Therefore, a comprehensive evaluation of the system, taking into account all relevant variables, is crucial to understanding the behaviour of gases in the experiment. To improve the performance of the microwave reactor chamber, numerical techniques outlined in Appendix E will be used to optimize its geometry, resolving issues related to electromagnetic fields and ensuring consistency in both thermal and electromagnetic fields across the sample. Furthermore, the impact of the material's dielectric constant on the distribution of the electric field within the sample will be studied, as described in reference [179]. These measures will result in improved operation of the microwave reactor chamber.

V.3 Effect of temperature measurement methods

Many published works on microwave heating report reaction temperatures that may be imprecise, and thus should be treated with caution. This is because the measurement process itself can change the distribution of electromagnetic waves, leading to disruptions such as absorption, reflection, or leakage. Furthermore, accurately determining the temperature at various points in the sample, such as the gradient between the surface of the crucibles and the core of the sample, can also be challenging. During our experiment, we encountered difficulties when attempting to measure the temperature inside the crucible using a thermocouple. Specifically, the measurement experiment failed, resulting in the thermocouple interacting with the microwave. This caused damage to one of the magnetrons, broke the crucibles, and corrupted the measuring device, as shown in Figure 42.



Figure 42. a) difficulty in removing the thermocouple from prepared crucibles; b) fracture in the inner crucible; c) crack in the outer crucible; d) quartz tube fusion with the pellets, which protects the thermocouple from its damage.

To minimize interactions and microwave leakage from the reactor chamber, it is crucial to keep the size and geometry of the temperature probe of the thermocouple as small as possible. To address the issues encountered in our previous experiment, we used non-contact methods such as an infrared digital pyrometer on the crucible side. However, obtaining accurate temperature measurements in microwave heating technologies can be difficult [217], and it requires a comprehensive understanding of microwave dielectric heating effects, as well as the development of temperature monitoring devices that use Artificial Intelligence to convert reflected microwave data into temperature measurements.

V.4 Effect of thermal expansion on temperature profile setup

The study of thermal materials at high temperatures is a common requirement for metallurgical research [218]. Crucible materials used in such research must be non-reactive to the different phases of the substance, free of impurities, and capable of withstanding high temperatures without dissolving or softening. Additionally, the crucibles must have the

necessary dimensions, shape, and capabilities, be highly durable, able to withstand thermal and mechanical shocks, and resist corrosive substances.

The development of crucibles and techniques for thermal analysis, such as dilatometry, is a crucial aspect of metallurgical research. To advance in this field, it is essential to continuously incorporate new experimental data into our understanding of these processes. In our study, we implemented a temperature profile configuration that took into account several key factors to ensure a successful experiment.

Firstly, we ensured that the chemical reaction for the sample would be achieved by carefully selecting the appropriate temperature range and duration of heating. Additionally, we took measures to protect the crucible from thermal effects by ensuring proper insulation and selecting a material with high thermal stability.

Another important aspect of our study was the protection of the welded parts of the reactor chamber during the cooling phase. This is crucial because failure to do so can result in thermal shock, which can lead to damage to the reactor chamber. In our case, the heating was accidentally turned off, and we noticed that the Eurotherm temperature controller failed to switch the cooling treatment processes to ones that matched the thermal weld properties. This resulted in a loss of welding resistance and cooling water leakage on electronic devices. Ultimately, this led to a loss of time and an increase in cost for repairing and manufacturing a new reactor chamber.

Furthermore, in the event of a welding defect, it is important to consider the design of the assembled structure of the reactor chamber for high-temperature and pressure experiments. This is because a poorly designed chamber can lead to further complications and ultimately affect the outcome of the experiment.

Overall, the development of crucibles and thermal analysis techniques is a complex process that requires a thorough understanding of the materials and processes involved. By continuously incorporating new experimental data and taking into account key factors such

as those mentioned above, we can improve the effectiveness and reliability of these techniques in metallurgical research. For example, Figure 43 shows a typical temperature profile for the reaction during a period of 120 minutes at 1800°C.



Figure 43. Temperature profile of a reduction experiment at 1800 °C is made up of one program with five different segments. A segment can include a temperature increase (1, 3), dwell time (2, 4), or decrease (5).

Programmable temperature controllers are industrial devices used to control the temperature of processes or machines where multiple controllers are required. These controllers are typically used in manufacturing processes, such as the production of silicon, glass, ceramics, and metals [219].

In these processes, it is critical to control the temperature to maintain the quality of the final product. The programmable temperature controllers can be integrated with software that allows for the coordination of data, such as gas flow and temperature. This is important because the correct ratio of gases and the correct temperature are essential for ensuring that the production process runs smoothly and efficiently. The software can be programmed to maintain the desired temperature range and adjust the gas flow accordingly.

In addition to coordinating data between the controllers, the software should also be able to monitor and control the thermal expansion of the crucible and the furnace chamber. Thermal expansion can cause damage to the crucible and furnace chamber, leading to production downtime and costly repairs. The software should be able to monitor and control the temperature in the furnace chamber to prevent thermal expansion and protect the equipment.

In summary, programmable temperature controllers play a crucial role in industrial and manufacturing processes by controlling the temperature of the process and coordinating data between multiple controllers. The software integration allows for precise control of temperature and gas flow and the protection of equipment from thermal expansion, improving the efficiency and safety of the process.

V.5 Effect of pellet size and additive on silica carbothermic reduction

The silica carbothermic reduction process, which is used to produce silicon, is known to be influenced by several factors, such as pellet size, composition, additives, temperature, and pressure. However, other factors such as the particle size of carbon and silica, and the ratio between them, also need to be considered and studied in order to fully understand their impact on the process [220].

The particle size of the reactants affects the heat and mass transfer rates, which in turn affect the reaction kinetics. The ratio between carbon and silica affects the thermodynamics of the process, as well as the stoichiometry of the reaction.

To investigate these effects, it is necessary to consider all technical and material factors that may have an impact on the process under microwave heat. This includes not only the variables previously mentioned but also other factors such as particle morphology, grain size distribution, and microstructure that may impact the process.

In industrial settings, the effect of these factors on the carbothermic reduction process can be studied using numerical modelling based on transport equations of momentum, energy, heat

transfer, solid phases, and other related physical phenomena [221]. These simulations can help to predict the internal phenomena occurring during the direct reduction process and aid in the optimization of the process for continuous silicon production.

The granulation of the silica and carbon mixture plays a crucial role in determining the efficiency and effectiveness of the carbothermic reduction process. The addition of binders such as polyvinyl alcohol (PVA) and water can improve the binding properties of the mixture, leading to a more uniform and stable reduction reaction. Furthermore, the size of the pellet has an impact on the reaction, as smaller pellets exhibit a higher surface area to volume ratio, which can result in an increased reaction rate.



Figure 44. Formation of silicon carbide in sample (a), partially reaction in sample (b), non-reacted pellets in sample (c), and formation of silicon phases in sample (d).

In our experiment, the results of the prepared pellets are presented in Figure 44 and summarized in Table 10, while the temperature measurements of the crucible samples are shown in Figure 45. The results indicate that Sample (a) underwent a complete reaction at 1496°C, whereas Sample (b) only partially reacted (65%) at 1361°C. The primary variables studied were the pellet size and microwave energy absorption, which are believed to have influenced the change in reaction percentages.

Sample (c) remained unreacted at 1252°C. This result indicates that there was not enough energy, or the reaction conditions were not sufficient to cause a reaction in sample (c). It

suggests that the reaction rate is highly dependent on the reaction conditions and that slight variations in these conditions can lead to significant differences in the reaction outcome.

The full interaction of the pellets was with the sample (d) when using PVA as a binder, where the temperature reached 1678°C. During this process, we noticed several colours as follows:

- Sample (d-A) exhibited a brown colour due to the presence of impurities and defects in amorphous silicon. These impurities alter its optical properties. Unlike crystalline silicon, amorphous silicon has a disordered atomic structure. The main cause behind the brown colour is the presence of silicon dioxide (SiO₂), a common impurity in amorphous silicon. SiO₂ can form through the condensation of silicon monoxide (SiO) gas generated during the deposition process. The presence of SiO₂ not only affects the optical properties of amorphous silicon, giving it a brown colour, but also its electrical properties, potentially impacting its performance in various applications. The specific shade of brown can vary depending on the type and amount of impurities and defects in the amorphous silicon.
- Sample (d-B) exhibited a grey metallic colour, which is attributed to the crystalline structure of silicon. Crystalline silicon possesses a well-defined crystal lattice structure and exhibits unique physical and chemical properties, including different electrical and thermal conductivity, as well as optical properties. The allotropy of silicon is influenced by the chemical bonding and crystal structure, which, in turn, is affected by the manufacturing conditions.

The observations on the different kinds of condensates found can lead to various interpretations of the formation mechanism. Further study of Reaction V.1, known as SiO disproportionation, and Reaction V.2, referred to as SiO synproportionation, can provide a better understanding of the conditions that contribute to the formation of specific phases and colours in silicon.

$$2SiO_{(g)} \rightarrow SiO_{2(s,l)} + Si_{(s,l)}$$
 V.1

$$SiO_{2(s,l)} + Si_{(s,l)} \rightarrow 2SiO_{(g)}$$
 V.2

This knowledge may potentially enable the control of phase and colour formations in future synthesis processes. Additionally, the condensation of SiO and CO during silicon production under an electric arc furnace can result in different colours, including crust, white, blue, and black [222].



Figure 45. Temperature measurement on the surface of the crucible samples, using a water binder for a) 5 mm pellets size (max 1496°C), b) 7 mm pellets size (max 1361°C), and c) 10 mm pellets size (max 1252°C); and using PVA binder for d) 5 mm pellets size (max 1678°C).

The weight loss of samples (a), (b), (c), and (d) was 85 g, 35 g, 9 g, and 150 g, respectively. Generally, weight loss is caused by the generation of CO, CO₂, and SiO gases. This weight loss indicates that gases were produced as a result of reactions, and the amount of weight loss varies depending on the percentage of reaction. Generally, the greater the percentage of reaction, the greater the weight loss. This suggests that the amount of weight loss could be used to predict the percentage of reaction, which would be useful for optimizing the control of industrial processes that use reaction progress as an indicator [223].

When comparing the results of samples (a) and (d) with the same pellet size (5 mm), it appears that the addition of PVA has a significant effect on silicon production from carbon and silica. PVA, on the other hand, can improve the integrity and stability of the pellet structure, prevent agglomeration of the carbon and silica particles, and allow for a more uniform distribution of the mixture. This results in more homogeneous reaction progress, which improves silicon production.

To differentiate between granulation, agglomeration, and pelletization, one should consider the different techniques used as well as the characteristics of the end products produced. Granulation is the process of bonding fine particles together with a liquid binder or a dry adhesive, resulting in irregularly shaped granules of varying sizes and densities. Agglomeration, on the other hand, is the process of compressing fine particles to form aggregates or clusters, which can lead to larger particles with irregular shapes and densities. Pelletization involves pressing or extruding small, uniform pellets or spheres, resulting in highly uniform particles with narrow size distributions.



Figure 46. Factors impacting pellet reaction under microwave radiation.

The reduction process under microwave heating is impacted by the shape and angles of pellets due to their effect on the reflection, penetration, and absorption of electromagnetic waves. Material and microwave factors also play a role in determining the reaction of pellets to microwave radiation, as depicted in Figure 46. Therefore, it is crucial to understand the influence of various factors for optimizing the reduction process.

In a study that used an induction furnace, Boucetta et al. [199] examined the impact of several binders on the reduction process. The researchers employed four different types of binders and found that using polyvinyl alcohol (PVA) and carboxymethyl cellulose (CMC) led to silicon yields of 33.8% and 27.8%, respectively. The use of PVA showed excellent strength of granules, and its capacity to endure the gas created during heating proved essential in averting explosions. Unfortunately, granules produced from starch and sucrose had low silicon yields due to minor CO gas explosions that occurred after heating.

On the other hand, Nagahata et al. [224] conducted a study to investigate the use of diatomaceous earth (DE) as a source of silica (SiO₂) by employing a microwave furnace. DE and graphite were suspended in an aqueous solution of polyvinyl acetate, which was used as the binder to form pellets for the reaction. The study found that under microwave irradiation, polycrystalline Si was produced at a lower temperature and shorter reaction time than with conventional arc-furnace methods. The energy-saving effect was attributed to the amorphous nature of DE, catalytic impurities, and selective heating by microwaves. By-products including SiC, β -SiO₂, and mullite were obtained. The optimal C/SiO₂ ratio for Si formation was found to be 1.0-1.5 at a temperature range of 1580-1680°C and a reaction time of 10-20 minutes using a microwave furnace.

Due to the microstructure interaction scale between silica and carbon particles within a single pellet, the heat transfer modes within a pellet can be approximately 20% conductivity, 30% convection, and 50% radiation, which are considered possible sources of unstable heat transfer ratios. Each pellet reacts differently when compared to pellets of the same size. This instability is caused by surface contact inhomogeneity and the ordered distribution of carbon

and silica particles. Even with the use of PVA, our microwave heating system achieved only 17% efficiency in silicon production.

Incorporating SiO₂/C, SiO₂/AC, and SiO₂/SiC composites can result in materials with unique and improved properties for absorbing electromagnetic waves [225, 226]. These materials have high electromagnetic wave absorption properties and can be used in a variety of applications, including radar-absorbing materials, stealth technology, and electromagnetic interference shielding. The unique structure and morphology of these composites contribute to their high conductivity and electromagnetic wave attenuation. Their high thermal stability and mechanical strength make them well-suited for use in harsh environments.

The understanding of the reaction mechanism is crucial for optimizing the high-energyconsuming process of silicon production. One promising approach to gaining insight into complex processes is through the study of chemical reactions using molecular dynamics (MD) simulations. These studies employ the reactive force field ReaxFF to simulate the reactions and provide a better understanding of the process [227, 228]. By using this method, we can create materials with improved properties such as high electromagnetic wave absorption, conductivity, and attenuation.



Figure 47. ReaxFF simulation: a) Reaction between cristobalite and amorphous carbon at 1950 K, b) Number of bonds. (JPM Silicon GmbH).

JPM Silicon investigated the ability of the ReaxFF force field to describe the various reactions that occur among solid, liquid, and gaseous compounds in the silicon production process. The team focused specifically on studying the reaction between silica and carbon and monitored
its progression by analysing the number and distribution of various bond types and angles, as illustrated in Figure 47.

Unexpectedly, the simulation did not produce any SiO molecules, in contrast to experimental findings documented in previous literature [229]. To further evaluate ReaxFF's potential to predict SiO formation, the team simulated the reaction between Si and SiO₂, which resulted in the formation of SiO molecules.

The simulated structures of SiO₂, SiC, Si, and C closely matched experimental values, suggesting that ReaxFF is a useful tool for investigating the SiO₂-C reaction system and uncovering the mechanisms that drive silicon production. Since 2011, the JPM Silicon team has successfully determined suitable parameters for studying chemical reactions in the system and conducted experimental studies on reaction temperature, resulting in silicon production in a microwave oven [230].

V.6 Raman analysis

The Raman analysis presented in this study involved analysing the Raman scattering spectra of samples (a, b, and d). The obtained Raman scattering spectra of these samples are shown in Figure 48.

In sample (a), analysis revealed the presence of peaks at around ~523 cm⁻¹, which were attributed to Si, and around ~794 cm⁻¹, which corresponded to the transverse optical (TO) mode of SiC. This mode was found to consist mainly of a cubic polytype structure, according to previous research [231, 232]. On the other hand, the Raman scattering spectra of sample (b) exhibited peaks corresponding to the TO phonon mode at around ~789 cm⁻¹ and a low-intensity longitudinal optical (LO) phonon mode at around ~973 cm⁻¹, which were attributed to SiC [231, 233]. In addition, the Raman analysis of sample (d) revealed that the dominant peak was located at around ~515 cm⁻¹ in position d-A (Figure 42), which corresponded to brown-coloured silicon. Another peak was observed at around ~517 cm⁻¹ in position d-B (Figure 44), which was attributed to metallic and greyish silicon [234]. These different colours

of silicon were found to correspond to the two allotropes of silicon, namely crystalline and amorphous silicon.





Compared to Raman analysis, powder morphology analysis provides complementary information on the physical and structural properties of powder samples. Raman analysis is a spectroscopic technique that can provide information on the chemical composition and molecular structure of materials. Powder morphology analysis, on the other hand, can provide information on the size, shape, and distribution of particles in a sample, as well as their surface features and defects.

Raman analysis and powder morphology analysis are important for the characterization of powder samples in metallurgy and materials science. They can provide information on the chemical composition, molecular structure, particle size, and shape of a material, which can be useful in the optimization of production processes and the development of new materials with improved properties. Overall, several analytical techniques are available to study the morphology of powders and mixed powders, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), optical microscopy, and laser diffraction particle sizing.

Conclusions and Perspectives

Conclusions

In this work, various important findings on the use of microwave technology for silicon extraction are presented. The influence of crucible position on heat distribution in microwave heating experiments, the precision of temperature measurement in microwave heating, the development of crucibles and thermal analysis techniques, and the carbothermal reduction process are important topics of study.

The use of a microwave oven is of great importance. Improves the efficiency of the carbothermal reduction process of silica. It was found that the crucible was effectively insulated using alumina foam bricks and aluminium silicate fibres. The distribution of electromagnetic energy within the oven chamber during microwave heating was found to be uneven, with the presence of cracks in the crucible being a significant contributor to temperature fluctuations.

Non-contact temperature measurement technologies, such as infrared digital pyrometers, may provide more precise results during microwave heating. Key issues for metallurgical research include carefully selecting appropriate temperature ranges, protecting crucibles from thermal effects, and selecting appropriate insulation and materials for reactor chambers.

The size of the pellet and the carbon-to-silica ratio have a significant influence on the reaction kinetics and thermodynamics of the carbothermal reduction process. Slight differences in the reaction conditions can lead to significant differences in the reaction results. By combining silica and carbon with water and polyvinyl alcohol as binders, pellets of different sizes were produced. Raman spectroscopy revealed peaks at 515 cm⁻¹ for silicon in polyvinyl alcohol pellets. at 523 cm⁻¹ and 794 cm⁻¹ for silicon and silicon carbide in water-bound pellets. The

size of the pellets has a significant impact on the absorption of microwave energy, with polyvinyl alcohol showing potential as a binder for silicon production in microwave ovens.

Our experiments successfully produced silicon through a microwave heating process using a mixture of silicon dioxide and carbon. It is important to note that many parameters affect the chemical reaction process, including pellet size, binder, and reaction temperature. Polyvinyl alcohol as a binder improved heat transfer and resulted in 17% efficiency in silicon production.

Based on the promising findings presented in this work, the remaining issues will be addressed in ongoing work and presented in future publications. Future efforts will focus on developing a new crucible to prevent silicon monoxide (SiO) gas loss during carbothermal reduction and achieve continuous production of solar-grade silicon under microwave irradiation.

Perspectives

The use of microwave technology provides a promising perspective for addressing challenges in the development of the solar-grade silicon industry and for the development of siliconbased batteries in future projects. The thesis findings highlight the potential of microwave technology in improving the efficiency of the carbothermic reduction process. This process can be significantly enhanced, resulting in higher throughput and more energy-efficient production. The reduction process is critical in the production of solar-grade silicon because it reduces costs and increases the availability of high-quality silicon for solar cell manufacturing.

Furthermore, microwave technology has the potential to benefit silicon-based batteries. Due to its high energy storage capacity, silicon is a promising material for next-generation batteries. However, one of the major challenges in using silicon in batteries is its significant volume expansion during lithiation, which can result in structural degradation and decreased battery performance. Microwave technology's precise control of heating and temperature distribution has the potential to alleviate this problem. By using microwave heating during the synthesis of silicon-based battery materials or during the charging/discharging processes, it

may be possible to achieve more uniform lithiation and minimize the negative effects of volume expansion. This can lead to better battery performance, higher energy density, and longer cycle life.

The goals outlined in the preceding perspective are linked to the valuable insights I gained through my participation in various projects, including the SSB project, which expanded my understanding of a major industrial company and the 3D planning mind-set. Furthermore, the JPM Silicon startup provided me with invaluable first-hand experience. Working with JPM Silicon gave me the opportunity to observe their successful business model of providing services to the university community, actively engaging with students, and sharing their experiences with them. This experience clearly demonstrated the importance and impact of these practices.

As a result of this experience, advancements will be made in enhancing microwave technology for academic and industrial purposes. These improvements will be documented and protected through a patent, with the intention of establishing a startup that caters to the university community. The primary objective of this venture is to offer a product that aids students in developing their skills in materials technology and supports them in establishing their own subsidiary startups. This initiative aligns with the policy of Algeria's Ministry of Higher Education and Scientific Research, which aims to foster innovative entrepreneurship among students pursuing a diploma or a startup diploma [235]. The collaboration for this endeavour involves the Algerian Ministry of Knowledge Economy, Startups, and Micro-Enterprises.

In general, the use of microwave technology appears to be a viable solution to the challenges associated with manufacturing solar-grade silicon and developing silicon-based batteries. As shown in Table 11, further research and development in this area can lead to a more efficient evaluation of scientific research results while incorporating educational objectives that align with student programs. To ensure the success of future student startup projects, departments such as Physics, Electrical Engineering, Mathematics, Computer Science, and the Institute of Applied Science and Technology must collaborate in one zone, similar to TMU's zone learning

model [236], to transfer knowledge and technology as incubators. Participation in the zone will result in job creation, industry stimulation, and economic growth.

Table 11. Program topics of course, research, and projects.

Bachelor degree	Year 1	Year 2	Year 3	Year 4
Course/Topic	Introduction to Materials Science	Materials Characterization	Introduction to Microwave Engineering	Advanced Topics in Materials Science
	Principles of Electrical Engineering	Circuits and Electronics	Materials Handling	Advanced Microwave Engineering
	Basic Chemistry	Thermodynamics	Digital Signal	Power Electronics
	Introduction to Programming	Data Structures, and Algorithms	Control Systems	Project-Based Learning
Master degree	Year 1		Year 2	
Course/Topic	Advanced Materials Characterization		Advanced Materials Processing	
	Advanced Microwave Techniques		Applied Electromagnetics	
	Battery Manufacturing		Project Management	
PhD degree	4 Years			
Research Topics/Projects	Development and optimization of a microwave-assisted silicon carbothermal reduction process for battery manufacturing and materials processing.			
	Development of novel microwave-assisted processes for materials synthesis and processing.			
	Investigation of the effect of microwave radiation on materials properties and its applications.			
	Development of startups in the field of microwave-assisted materials processing.			

Finally, it is crucial to establish external partnerships with various institutions, such as the National Institute of Innovation Management in Algeria, to create a common understanding. This will help to train and support individuals with innovative ideas, as well as executives in the economic sector. Additionally, it is important to partner with the passionate Algeria Venture team, which is dedicated to accelerating the country's aspirations in industrialization, entrepreneurship, digitization, and more. This approach will create job opportunities, promote environmental protection, initiate a cultural movement, and integrate minorities into development processes. It is also worth mentioning the support provided by the Algerian Startup Fund (ASF), where there is a strong correlation between venture capital funding and the financial success of innovative projects, contributing to the success of many startups [237].

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Appendices

Appendix A. Thermodynamic calculations

• Reaction equilibrium

The reaction equilibrium constant K_x is linked as a function of temperature and pressure via the chemical potential with the free enthalpy of reaction ΔG , so that:

$$K_{\chi}(T,p) = \exp(-\frac{\Delta G^{\circ}}{RT})$$
 A.1

For the reaction between quartz and carbon according to reaction II.3:

$$SiO_2 + C = SiO + CO$$

As example at temperature of 1650°C (1923 K) and a pressure of 1 atm:

 Standard Gibbs free energy change (ΔG°) can be calculated using the standard enthalpy and entropy changes (ΔH° and ΔS°), using the equation:

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$$
 A.2

The values for ΔH° and ΔS° for the reaction can be obtained from thermodynamic databases or experimental measurements. For this reaction:

 ΔH° = -185.54 kJ/mol, ΔS° = 205.27 J/mol·K

Converting ΔH° to J/mol and substituting the values, we get:

• Equilibrium constant K_x (T,p) can be calculated using the equation A.1, where R is the gas constant (8.314 J/mol·K), T is the temperature in Kelvin (1923 K), and ΔG° is the standard Gibbs free energy change for the reaction II.3 (-355.20 kJ/mol). Substituting the values, we get:

$$K_x = \exp(-\Delta G^{\circ}/RT) = \exp((-355200 \text{ J/mol}) / (8.314 \text{ J/mol} \cdot K * 1923 \text{ K})) = 1.15 \cdot 10^{24}$$

• Equilibrium constant K_p can be calculated from K_x using the equation

$$K_p = K_x * (\mathsf{RT})^{\Delta \mathsf{n}} \tag{A.3}$$

where Δn is the difference in the number of moles of gas between the products and reactants. For the reaction II.3, $\Delta n = (1 + 1) - (1 + 1) = 0$. Substituting the values, we get:

$$K_p = K_x * (\text{RT})^{\Delta n} = 1.15 \cdot 10^{24} * (8.314 \text{ J/mol·K} * 1923 \text{ K})^0$$

 $K_p = 1.15 \cdot 10^{24}$

• However, at equilibrium, the amount of SiO_2 is constant since it is a solid, and the partial pressure of C is very small compared to the partial pressures of SiO and CO. Therefore, we can assume that the product of P_{SiO_2} and P_C is negligible compared to the product of P_{SiO} and P_{CO} . This allows us to simplify the expression and the equilibrium partial pressure of SiO can be calculated using the equation:

$$K_p = (P_{SiO} * P_{CO}) / (P_{SiO_2} * P_C)$$

Please note that after determining the appropriate values of temperature, pressure, and K_p for the reactions system, the experiment can be set up in the microwave furnace. Additionally, it is necessary to use appropriate analytical techniques, such as gas chromatography or quadrupole mass spectrometry, to monitor the progress of the reaction. It's worth mentioning that microwave heating can sometimes result in non-equilibrium conditions. Therefore, it's crucial to monitor the reactions carefully and ensure that equilibrium has been reached before analyzing the products.



Figure A1. Free energy change (ΔG) of the possible SiO₂-C reactions [203, 204].

• Mechanism of reaction of silica and carbon

The accuracy of the results in TGA experiments can be affected by small amounts of the carbon-silica mixture because the reaction mechanisms may change at different scales. In smaller quantities, the reaction kinetics and heat transfer can differ from those in larger scale reactions, leading to differences in the reaction pathways and thermal behavior of the materials. Furthermore, small sample sizes can also affect the resolution and sensitivity of the TGA instrument, which can impact the accuracy of the data obtained. Therefore, the results obtained from TGA experiments on small quantities of the carbon-silica mixture should be interpreted with caution and may not be directly applicable to larger scale reactions.




Appendix B. Instruments microwave accessory

(Fricke und Mallah Microwave Technology GmbH)

• Power Supply

- Power Output: 6 kW.
- Line Input 3 Phase 400 / 440 / 575 V_{AC}.
- Line Frequency 50 Hz / 60 Hz.
- Input Power 9.92kVA @ 400V_{AC}.
- Maximum intake current 15.3A @ 380V_{AC}.
- Ripple ≤ 2 % of output power.
- Ambient Temperature Up to 40°C max.
- Air Cooling, Intake airflow Appx. 300 m³/h.
- Dimensions (482 x 311 mm) depth (660 mm).

Magnetron Head

- Output Power 6kW.
- Fixed Frequency 2450 +/-10 MHz.
- Filament Voltage 5 +/- 0.2 V_{AC} .
- Filament Current 29 A_{AC}
- Water Cooling: max. 500 kPa, > 4 l/min, +18°C.
- Dimensions (WxHxD) 310 x 248 x 390 mm.

• Circulator / Isolator 6 kW

- Frequency 2425 ... 2475 MHz.
- Isolation min 23 dB.
- Insertion loss max 0.15 dB.
- Return loss min 23 dB.
- Power (forward) 6.5 kW cw.
- Power (reflected) 6.5 kW cw.
- RF leakage < 0.5 mW / cm 2 .
- Dimensions (WxHxD) 194x310x115 mm.







• Water Load

- Water loads are compact.
- Water inlet temperature +10°...+40° C.
- Water outlet temperature max +SO° C.
- Storage temperature -10°...+10° C.
- Static water pressure max 600 kPa.

• Tuners

- Manual 3-Stub-Tuner:
- Frequency range 2400 2500 MHz.
- max. Power Handling 20 kW.
- Dimensions WxHxL 138x203x260 mm.

• Auto-Tuner:

- Frequency range 2400 2500 MHz.
- Maximum working powe 100 W 30 kW.
- Dimensions WxHxL 138x203x260 mm.

- For further information, consulte the company's data sheet (FM-AT-3S/2450).

• Power measurement system

- Frequency Range 2400 2500MHz.
- Absolute maximum RF input power 70 dBm (10 kW).
- Waveguide Flange of the Directional.
- Measurement Unit Size 140 x 400 x 200 mm.
- PC connection: USB Type A.









Appendix C. Raw materials and pellets preparation

• weigh reaction mixture

For a total weight mixture of W_{mix} (200 g), mass balance of 3 moles silica (its molar mass is 60 g/mol) and 2 moles carbon (its molar mass is 12 g/mol) are:

$$W_x = \frac{W_{mix}}{x+y} \cdot x$$

$$W_{mix} = W_{SiO_2} + W_C$$

$$x = 3SiO_2 = 3 \ mol \cdot \left(60 \frac{g}{mol}\right) = 180g$$
$$\Rightarrow W_{SiO_2} = \frac{200g}{180g + 24g} \cdot 180g$$

$$\Rightarrow W_{SiO_2} = 176.47 \ g$$
 of Silica

$$y = 2C = 2 \mod \left(12 \frac{g}{\mod} \right) = 24g$$
$$\Rightarrow W_C = \frac{200g}{180g + 24g} \cdot 24g$$
$$\Rightarrow W_C = 23.53 \ g \text{ of Carbon}$$

• Disc granulator

The critical speed is an essential operating parameter for the disc. This is defined as the speed at which a granule is held immobile on the rim of the disc only by centripetal forces, (Figure. C1).

$$N_c = \sqrt{\frac{g\sin\beta}{2\pi^2 D}}$$

Discs generally operate between 50 and 75% of critical speed with an angle β between 45 and 55°. If the speed is too low, the mass of particles will slid against the disc rather than fall. If the speed is too high, the particles are glued to the rim or can be ejected out of the disc.



Figure. C1. Left, force equilibrium on a pellet with a critical speed disc [205]. Righi, disc granulator

with a dry heating system (AS ONE Corporation, Japan).

Disc granulator data sheet (AS ONE Corporation, Japan) [206].					
Features	Specification				
 Angle, rotation, and time setting is the rotation granulator of freely pan dia. 240*mm*. Useful in small amount of granulated sample making. It is granulator of capacity in, up pan diameter and rotation torque peripheral speed of pan granulator DPZ-01R. Rotation speed timer is possible precise setting in digital. It is medium-capacity pan granulator type equipped with a drying function to PZ-02R. Even if too hydrolysis during granulation can be water-reducing in the dry. It is double outside with plate to eliminate the touch of a high temperature. 	 Size (mm): 540 x 373 x 630 (when 45° angle) Weight (kg): 14.3 Pelletization method: Snowman method due to rotation (left rotation) Rotation speed: 20 - 112rpm Timer: 0 - 9 hours 59 minutes (1 minutes units) Material: Body/SPCC (steel plate) white leather tone coating, Pelletization container/stainless steel (SUS304) Safety device: Overcurrent protection, glass tube fuse 0.5A Pelletization container inner dimensions: \$\phi300 x 120mm\$ Obliquing angle: 90° (horizontal to vertical) Heater function: Heater/60W, Heater control method/bimetal timer. Power supply: 100VAC 50/60Hz Power cord length: 2.5m Processable amount: 1kg (when 45° angle) Motor: 10W Model number: DPZ-01R 				

• Air jet mill

The Air jet mill [207], as depicted in Figure C2, is a technique for size reduction and classification that uses high-speed air streams to grind powders into fine particles. The technology is equipped with a closed-loop system, which provides precise control over particle size and size distribution.

The closed-loop system in the air jet mill continuously monitors the particle size of the powders and makes adjustments to the process as needed. This ensures that the final product meets specific size and quality requirements, improving product quality, and enhancing production efficiency. Additionally, air jet milling utilizes high-speed air streams to reduce processing times and increase overall production capacity.



Figure C2. Overview of the grinds and powder classifications to micron and sub-micron sizes by jet mills (Sturtevant, Inc. HQ).

Overall, air jet milling technology offers a reliable and efficient method of size reduction and classification. Its closed-loop system and ability to provide precise control over particle size and size distribution, along with enhanced production efficiency, make it a valuable tool for manufacturers seeking to improve their production processes, and scale up the development of the industry.

Appendix D. Instrument analysis

• Laser Raman spectrometer

- Laser wavelength: 532.08 nm, 632.80 nm, 100 mW Laser safety interlock mechanism
- Spectrometer: 300 mm (with low wavenumber measurement attachment)
- Analysis grid: Porografic analysis grid, 1800 gr/mm
- resolution: Approx. 1 cm⁻¹
- wave number Range: 10 to 8000 cm⁻¹ (Raman shift value)
- Detector: High sensitivity CCD



Figure D. Laser Raman spectrometer JASCO, NRS-3300 (Nagoya Institute of Technology)

The NRS-3300 spectrometer is a versatile tool designed for ultra-low wavenumber range measurements, offering high resolution and sensitivity. It is well-suited for Raman analysis and broadband qualitative analysis due to its low wavenumber measurement attachments and ability to select the optimal equipment configuration, including the excitation laser wavelength for resonance effect or fluorescence avoidance. The high-precision direct-drive system provides reliable performance, while automatic configuration switching and auto-alignment functions enhance the spectrometer's operability and maintainability.

However, the NRS-3300 device does have limitations and cannot accommodate samples taller than 2 cm.

Appendix E. List of numerical methods available

Table 12. List of numerical methods available [216]

Modelling microwave power problems					
Numerical Method	Advantages	Limitations	Applied software	Applied research work in microwave power engineering	
Finite Difference Time Domain (FDTD)	 Ability to obtain wideband results. Quick implementation on parallel computers. Good at modelling inhomogeneous and complex materials. Computational memory required less. 	 Errors are dispersive for larger time steps. Difficult to model thin metal pieces. Difficult to model materials with frequency dependent properties. 	 Quickwave 3D 7.5 Empire XCcel 5.40 XFDTD 7.0 FIDELITY 3.0 	 Ma et al. 1995 Mechenova and Yakovlev, 2004. Kopyt and Celuch, 2003 Kopyt and Celuch, 2004 Kopyt and Celuch,2007 Tilford et al. 2007 Wäppling-Raaholt et al. 2002 Chen et al.2008 	
Finite Element Method (FEM)	 Good at handling complex geometries. Can handle wide variety of engineering problem. Easy to implement frequency, thermal, pressure, and force dependent material properties. Best method for modelling resonant cavities. 	 It obtains only approximate solution. Large computational memory required. Absorbing boundary required for radiation problem. 	 HFSS 12.0 Multiphysics 12.1 (ANSYS) COMSOL Multiphysics 4 Abaqus 6.8 LS-DYNA (also available in MOM) EMAS (Ansoft Corp.) NASTRAN ALGOR TWODEPEP(ANSYS) 	 Kopyt and Celuch, 2004 Kopyt and Celuch, 2006 Ehlers and Metaxas, 2007 Zhang et al. 2001 Zhang and Datta, 2003 Akarapu et al. 2004 Pandit and Prasad, 2003 Huo and Li, 2005 Zhou et al. 1995 	

Appendices

Modeling microwave power problems (Continued)

Transmission Line Method (TLM)	 Analysis is performed in time domain. Absorbing boundary condition can be easily modelled. System explicitly solved. 	 Requires more computer memory than FDTD method. 	 MEFiSTo-3D Pro 2 Micro- Stripes 5.6 	_
Finite Volume Method (FVM)	 It is well suited for implementing in unstructured meshes. Electromagnetic field values calculated for a small volume which represents more accurate value of the small domain. It is well suited for flow dynamics equation solving. 	• Dispersive errors more in surface integrals.	 Fluent 13.0 EMC2000-VF FLOW-3D 8.2 CFX 4.3 PHOENICS 	 Kopyt and Gwarek, 2004 Kopyt and Celuch,2006 Kopyt and Celuch,2007 Verboven et al. 2003 Dincov et al. 2004
Method of Moments (MOM)	 It can be used to solve a wide range of equations involving linear operations. It is highly useful method to solve large and dense matrix equations. 	 It is only best suited to solve for linear equations not for non-linear problems. 	• CONCEPT II 8.0	-
Boundary Element Method (BEM)	 Accurate modelling of infinite and semi-infinite domains. Discretization required only for boundary not for entire domain. 	 It does not model well for inhomogeneous or complex materials. Not good for modelling the problems that combine small details geometries with larger objects. Practical application not well established. 	• LS-DYNA	• Huo and Li, 2005

Modelling electromagnetic and thermal fields (Continued)

Modelling electromagnetic and thermal fields					
Simulation package (Electromagnetic and Thermal)	Numerical method	Features	Supplier	Applied research work in microwave power problem	Applications
High Frequency Structure Simulator (HFSS) 12.0 *	FEM	 Automated solution process. Fast and accurate s-parameter extractions. Automatic mesh generation and adaptive refinement. Domain decomposition (a job can be distributed into multiple network computers). Adoption of curvilinear elements and mixed element orders. 	• Ansoft Corp. www.ansoft.com	-	 Microwave and radio frequency analysis Signal integrity and chip development
Multiphysics 12.1 **	FEM	 Unified simulation environment for solving multi –physics disciplines. Importing CAD geometries. Support for parallel processing. Support for dissimilar mesh interface between physics models. Includes non-linear geometric effects. 	• ANSYS Inc. www.ansys.com	• Yakovlev,2001a Geedipalli et al., 2007	 High frequency electromagnetic analysis Thermal and fluid flow analysis Structural analysis Circuit design
Microwave studio 5.0 *	FIT	 Perfect boundary approximation. Multilevel subgridding scheme. Optimization strategies for multiple parameters 	 Computer Simulation Technology (CST) www.cst.com 	• Yakovlev,2001a Akhtar et al. 2008	 Microwaves and radio frequency Statics and low frequency Biomedical Signal integrity

Appendices

Modeling electromagnetic and thermal fields (Continued)

Empire XCcel 5.40 *	FDTD	 Frequency dependent loss modelling. 3D arbitrary shape import/export. Multi-core CPU supports. Object parameterization. 3-D video display of field distributions. 	• IMST, GmbH www.imst.com	-	 Microwave and radio frequency component design Antenna design Circuit design Automobile industry
XFDTD 7.0 *	FDTD	 GPU acceleration for fast computing. Script library to automate the modeling. Complete parameterization control. Customizable results browser. Designed to run Windows, Mac OS X, and Linux platform (only EM software compatible to all platform) 	• Remcom Inc. www.remcom.com	-	 Antenna design Microwave circuits design Wireless communications Lens design
COMSOL Multiphysics 4.0 **	FEM	 Global definition of model variables. Streamlined model builder. In-built model library for common applications. Sweeping parameter geometry. Options for parallel computing. More boundary conditions options for thermal analysis. 	• COMSOL Inc. www.comsol.com	 Curet et al. 2006 Romano et al. 2005 Knoerzer et al. 2008 	 Chemical Engineering Microwave and radio frequency power engineering Acoustics Earth science Batteries and fuel cell design
QuickWave 3D 7.5 **	FDTD	 Conformal FDTD meshing. Parameterization of model geometry. Coupling to computational fluid dynamics software. Importing CAD figures. Options for multi-simulation. S-parameter extraction. 	• Qwed Sp. Z.o.o. www.qwed.com.pl.	 Mechenova and Yakovlev, 2004 Celuch and Gwarek, 2007 Tilford et al. 2007 Chen et al.2008 Knoerzer et al. 	 Microwave power engineering Antenna design

Appendices

Modelling electromagnetic and thermal fields (Continued)

ANSYS Fluent 13.0 ***	FVM	 Unstructured mesh can be adopted for complex objects. Dynamic and moving mesh adoption. Parallel processing with other CFD platforms. Options for exporting simulations in data and animations format. 	• ANSYS Inc., www.ansys.com	 Kopyt and Gwarek, 2004 Kopyt and Celuch,2006 Kopyt and Celuch,2007 	 Fluid flow analysis Thermal analysis Acoustics
Abaqus 6.8 ***	FEM	 Structural finite element analysis (FEA) (same model information can be used for multiple physics). Direct coupling to 3rd party software and independent-code. 	• Dassault Systems www.simulia.com	-	 Structural Analysis Automobile Industry Electrical circuit analysis Flow dynamics Acoustics

FDTD – Finite Difference Time Domain Method; FEM – Finite Element Method; FVM- Finite Volume Method; FIT- Finite

Integration Technique. * - Electromagnetic solver; ** - Electromagnetic and thermal solver; *** - Flow dynamics solver.

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Effect of pellet size and additive on silica carbothermic reduction in microwave furnace for solar grade silicon

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Silicon as a raw material for solar cells can be produced by numerous methods. The carbothermic reduction of silica using electric arc furnace is the most widely used process in silicon industry. This paper presents a new approach to produce solar grade silicon using microwave furnace. Pellets of different sizes were prepared from a mixture of silica and carbon using water and polyvinyl alcohol as binder agents. Raman spectra indicated a peak at about 515 cm^{-1} attributed to silicon in the pellets prepared with polyvinyl alcohol, and peaks at about 523 cm^{-1} and 794 cm^{-1} attributed to silicon carbide, in the pellets prepared with water. The pellet size affects the absorption of microwave energy emitted from the magnetrons. Polyvinyl alcohol as a binder agent is promising for the production of silicon using microwave furnace.

Keywords: microwave furnace; carbon; silica; solar grade silicon; solar cells

1. Introduction

For more than 100 years, the process of silicon production has been in continuous development for application in electronic chips and solar panels. Several research projects have been conducted to produce low cost silicon for the photovoltaic industry [1].

Carbothermic reduction is a common industrial procedure to manufacture solar grade silicon from silicon dioxide (SiO₂) in an electric arc furnace according to the simplified reaction equation:

$$SiO_2 + 2C \longrightarrow Si + 2CO$$
 (1)

The reaction in equation 1 seems to be the overall reaction for silicon production. Moreover, many chemical reactions with different stoichiometry are possible in the reaction system between silica and carbon (–) as shown in Table 1. Nevertheless, the reaction mechanisms are still being researched and developed in order to find new processes, which require the knowledge of how to control this complex reaction system between solid, liquid and gaseous matter, as illustrated in Table 1, and to increase the energy efficiency process during silicon production. Heating a mixture of silica and carbon (mole ratio 1:2) produced silicon carbide (SiC) and silicon monoxide (SiO) but not silicon [2].

Therefore, the reduction of SiO_2 with C, at high temperature, may form silicon monoxide (SiO), carbon monoxide (CO) and silicon carbide (SiC) as shown in Table 1. Where, g, l and s correspond to gas, liquid, and solid phases, respectively. As the reaction in equation 2, equation 3 and equation 5 can be controlled by the amount of silicon monoxide, so it is assumed that SiO is the most important reactant by-product in silicon production. Moreover, the analyses of gas phases using Q-mass spectrometer cannot detect SiO gas but only CO

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(6)

Table 1. Possible reactions between SiO₂–C during heating process.

Reaction equation

- $$\begin{split} SiO_2 + 2C &\rightarrow Si + 2CO \qquad (1)\\ SiO_2(s) + C(s) &\rightarrow SiO(g) + CO(g) \qquad (2)\\ SiO(g) + 2C(s) &\rightarrow SiC(s) + CO(g) \qquad (3)\\ 2SiO_2(s) + SiC(s) &\rightarrow 3SiO(g) + CO(g) \qquad (4) \end{split}$$
 - $SiO(g) + SiC(s) \rightarrow 2Si(s) + CO(g)$ (5)
 - $SiO_2(l) + Si(l) \rightarrow SiO(g)$

gas. In addition, a new method was used for weight loss of SiO and CO gases [3]. As the chemical reaction in equation 4 shows, the silicon carbide can enhance the silicon production yield [1], and it can prevent the loss of SiO gas as shown in the reaction equation 5. In turn, silicon monoxide (SiO) is an important element to increase the amount of silicon.

The chemical reactions that occur during the carbothermic reduction of silica depend not only on the raw material properties but also on different heating sources and their interactions with the materials [4]. In this paper, we developed an approach for solar grade silicon production using microwaves as a heating source. Amorphous carbon such as activated carbon, coke, charcoal, and coal represent good microwave absorbers. Thus, we used carbon for heating and reaction in the microwave processes. The main advantages of this process are safety, ease to manipulate, and fast heating. The results of the analysis show the advantages for silicon production.

The following part of the paper is organized as follows: Section 2 describes an experimental study that we conducted during our research. In Section 3, we discuss our results and, finally, Section 4 summarises the results of this work and draws conclusions.

1.1. Microwave heating theory

The idea of microwave heating is to dissipate the energy of microwave by converting it into heat, depending on the properties of a material and its ability to absorb microwave energy [5].

Materials are classified into three different groups when exposed to microwave irradiation: microwave absorbers (silicon carbide, charcoal and activated carbon), microwave transparent (alumina, quartz), and microwave reflectors (solid metals) [6].

The properties of materials and their ability to absorb the power of microwaves depend on how they store the energy, which is connected with a dielectric constant and how they dissipate energy which is connected with dielectric loss. The ratio of these two factors is defined by the loss tangent tan and the relative permittivity [7] according to the following equation:

$$\tan \delta = \frac{\varepsilon_r''}{\varepsilon_r'} \tag{7}$$

In general, frequency dependence of dielectric constant and dielectric loss in some materials is strongly influenced by temperature [8]. Knowing the properties of a material allows us to predict its ability to absorb the energy supplied by magnetrons. The average power absorbed by a certain amount of material when heated dielectrically is expressed as [9]:

$$P = 2\pi f \varepsilon_0 \cdot \varepsilon_r \tan(\delta) E^2 \tag{8}$$

where is the dissipated power [W/cm³], the energy source is represented by the electrical field strength [V/cm] and is frequency [Hz]; the dielectric constant and the loss tangent are the material properties. Generally, for industrial microwave furnaces, the frequency fis equal to 2.45 GHz [10].

F

When a microwave radiation penetrates a material, such as a dielectric, an energy loss occurs, because the thermal conductivity of the material depends on the absorption and penetration depth of microwave energy, and then, as thermal conductivity increases, heat dissipation also increases [11]. To determine the uniformity of heating and the depth of the microwaves penetration into a material, it is important to know the dielectric properties of the material [9, 12]. The penetration depth of microwave energy from the surface to the bulk of material is defined as the depth at which the power decreases by half its value [9, 13, 14] In this work, 124

the results show that the penetration depth is influenced by the pellet size, homogeneity of powder mixture and the additive of polymer.

2. Experimental study

2.1. Heating mechanism

Microwave heating systems in the industrial sector differ from each other depending on their applications. As shown in Fig. 1, the microwave system used in this study includes microwave power supply, magnetron head, cooling system, and waveguide components (isolators/circulators, tuning system and waveguides).



Fig. 1. Schematic illustration of multi-mode microwave heating system.

The sample is heated in a multi-mode microwave furnace by four magnetrons ①, each having a variable microwave power with a maximum value of 3 kW at a frequency of 2.45 GHz. The tuning system 3 is used to reflect unabsorbed microwaves into the furnace chamber ④ and increase energy efficiency. Moreover, circulators 2 are used to protect the magnetron from reflected microwave energy by a three-port device system using ferrite technology (magnets), typically circulators combined with a water load, which has a high power absorption capacity. The temperature is measured by infrared thermometers ⁽⁵⁾. The experiments were carried out according to the heating profile after removing all the air from the chamber using a rotary pump to avoid oxygen oxidation and injecting of an inert gas such as argon (Ar).

2.2. Sample

The study aims to investigate the effect of pellet size on the carbothermic reduction of silica sand by microwave irradiation. We have used 3 moles of powdered crystalline silica (SiO₂) (average particle size of 63 μ m, Kojundo Chemical Lab. Co., Ltd., Japan) mixed with 2 moles of black carbon (average particle size of 20 μ m, Kojundo Chemical Lab. Co., Ltd., Japan), using a mortar and pestle.

Then, we made the pellets with different sizes from the mixed powders and dried them at 80 °C for 90 minutes in a pan. We compared two different binder agents: water and polyvinyl alcohol (PVA) [-CH₂CHOH–]_n (Aldrich Chemical Company, USA), as shown in Table 2.

An alumina crucible was used to preserve the prepared pellets, as microwave irradiation does not affect this material which is considered as transparent. The intensity of microwave radiation depends on the design and geometry of the furnace chamber, thus, the crucible must be placed inside the chamber at the point of high concentration of microwave irradiation [15]. Moreover, to avoid energy loss, we used an insulating alumina fiber blanket to cover the crucible. The experiments were carried in an inert atmosphere of Ar gas under a pressure of $\sim 10^5$ Pa.

During the experiment, an infrared thermometer, with a temperature range of $400 \,^{\circ}$ C to $2500 \,^{\circ}$ C, was used to measure the temperature on the crucible side. Unfortunately, we were unable to use a thermocouple to measure temperature because it causes damages to samples when they are exposed to microwave irradiation [15].

Instead, simulations of the electromagnetic field distribution with the temperature profile can be used to predict the temperature of the mixture inside the crucible during microwave heating of the carbothermic reduction of [16, 17].

3. Results and discussion

The samples after reactions are presented in Fig. 2. Sample a reacted completely at 1496 °C, however, sample b reacted partially (65 %) at 1361 °C. Sample c remained unreacted

е 1

Table 2. Raw materials for pellets preparation

Sample	Mixture [g] SiO ₂ –C	Binder agent	Pellets size [mm]	Ratio of binder by weight [%]
(a)	200	water	5	10
(b)	200	water	7	10
(c)	200	water	10	10
(d)	200	PVA	5	3



Fig. 2. Formation of silicon carbide in sample a, partial reaction in sample b, non-reacted pellets in sample c and formation of silicon phases in sample d.

at a temperature of 1252 °C. The change of the reactions percentages was due to the effect of pellet size and the microwave energy absorption. In sample d, the temperature increased to about 1678 °C. As shown in Fig. 2d, there are many colors: brown, grey metallic and green. The green color corresponds to silicon carbide, brown and metallic grey correspond to different phases of silicon according to the manufacturing conditions [18]. The weight loss of the samples a, b, c and d was 85 g, 35 g, 9 g, and 150 g, respectively. In general, weight loss was caused by the generation of CO, CO₂ and SiO gases [3].

3.1. Raman analysis

Raman spectrometer used in our research was (NRS-3300, Jasco, USA). Fig. 3 shows the Raman scattering spectra of sample a, sample b and sample d. In sample a, we notice the presence of peaks at \sim 523 cm⁻¹ which can be attributed to Si, and \sim 794 cm⁻¹ referred to the transverse optical (TO) mode of SiC which consists mainly of a cubic polytype structure [19, 20]. In sample b, the observed peaks correspond to the TO phonon mode at \sim 789 cm⁻¹, and low intensity longitudinal optical (LO) phonon mode at \sim 973 cm⁻¹, attributed to SiC [19, 21].

Moreover, as shown in Fig. 2d, the dominant peak observed is located at \sim 515 cm⁻¹ in position A which corresponds to brown colour silicon, and another peak observed at \sim 517 cm⁻¹ in position B can be attributed to metallic and greyish silicon [22]. These different colors of silicon correspond to the two allotropes of silicon, i.e., crystalline and amorphous silicon.

4. Conclusions

In conclusion, following our experiments we succeeded to produce silicon by a microwaveheating process using a mixture of silica and carbon. It is important to note that many parameters influence the chemical reaction process such as pellet size, binding agent and reaction temperature. Polyvinyl alcohol as a binder agent improved heat transfer and resulted in a 17 % efficiency in silicon production.

On the basis of the promising findings presented in this paper, work on the remaining issues 126

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Fig. 3. Raman scattering spectra of samples a, b and d.
(a) peak at 523 cm⁻¹ corresponds to silicon and peak at 794 cm⁻¹ corresponds to silicon carbide,
(b) peaks at 789 cm⁻¹ and at 973 cm⁻¹ correspond to silicon carbide, (d-A) peak at 515 cm⁻¹ corresponds to silicon, (d-B) peak at 517 cm⁻¹ corresponds to silicon

is continuing and will be presented in future papers. Therefore, we intend to make a new crucible design to prevent silicon monoxide (SiO) gas loss during the carbothermic reduction, and to achieve continuous production of solar grade silicon under microwave irradiation.

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