Polymer Infiltration and Pyrolysis of Silicon Carbide Ceramics

Using Transient Liquid

by

Anqi Wang

BS, Nanjing University, 2015

MS, University of Pittsburgh, 2018

Submitted to the Graduate Faculty of the Swanson School of Engineering in partial fulfillment of the requirements for the degree of Doctor of Philosophy

University of Pittsburgh

2023
UNIVERSITY OF PITTSBURGH

SWANSON SCHOOL OF ENGINEERING

This dissertation was presented

by

Anqi Wang

It was defended on

Nov 07\textsuperscript{th}, 2023

and approved by

Ian Nettleship, PhD, Professor, Department of Mechanical Engineering and Materials Science

Wei Xiong, PhD, Professor, Department of Mechanical Engineering and Materials Science

Stephen House, PhD, Professor, Department of Chemical and Petroleum Engineering

Young Jae Chun, PhD, Professor, Department of Industrial Engineering

Dissertation Director: Jung-Kun Lee, PhD, Professor, Department of Mechanical Engineering and Material Science
The polymer infiltration and pyrolysis (PIP) method has a limitation in increasing the density of SiC ceramics after multiple PIP cycles. This is due to an increasing number of blocked pores that decreased the amount of polymer infiltrated deep into the interior of bulk materials. In this study, a new process that incorporates Ni and carbon nanoparticles into SiC polymer precursor is examined. Ni and carbon nanoparticles were uniformly distributed into porous SiC ceramics during the polymer infiltration. The reaction of nanomaterials with SiC polymer precursor results in a transient liquid phase during the pyrolysis, which mitigates the pore closure. Ni nanoparticles reacted with the SiC precursor to form a nickel silicide of low melting temperature such as Ni$_2$Si and NiSi phases. During high temperature pyrolysis, these silicide phases turned to a liquid phase, facilitated the redistribution of the infiltrated material, and maintained the pore structure open. In later infiltration steps, the co-addition of carbon nanoparticles into the polymer precursor helps the conversion of nickel silicide to nickel carbide and decreases the amount of residual nickel silicide which may be harmful for mechanical strength at high temperature. Results of this study show significant improvement in the density of SiC ceramics in comparison to traditional PIP.
# Table of Content

Chapter 1 Introduction

1.1 SiC Ceramics: Material Properties And Applications

1.1.1 Crystal Structure And Mechanical Properties of SiC

1.1.2 Application of Mechanical Properties of SiC

1.1.3 Application of Electrical Properties of SiC

1.2 Processing of SiC Ceramics

1.2.1 Traditional Sintering Process of SiC

1.2.2 Reaction Sintering

1.2.3 Polymer Infiltration

1.3 Additive Manufacturing of Ceramics

1.3.1 Binder-jet Printing

1.3.2 Selective Laser Sintering (SLS)

1.3.3 Digital Light Processing

1.4 Challenges of SiC Sintering Technique And Current Problems of AM Technique

1.5 Hypothesis and Objective

Chapter 2 Enhanced Densification in The Polymer Infiltration Process of SiC Using the Formation of Liquid Phase

2.1 Introduction

2.2 Experiment

2.3 Results and Discussion

Chapter 3 Effect of carbon additives in PIP process of nanoparticle added SiC densification

3.1 Introduction

3.2. Experiment

3.3 Result and Discussion
Chapter 4 Advanced Densification Technique on SiC Binder-Jet Printing Matrix via Polymer Infiltration and Pyrolysis .......................................................... 65

4.1 Introduction .................................................................................. 65

4.2 Experiment .................................................................................. 73

4.3 Results and discussion ................................................................. 77

4.4 Conclusion .................................................................................. 92

Chapter 5 Overall Conclusion ................................................................. 94

Bibliography .................................................................................. 96
# Table of Figures

| Figure 1.1 | SiC lattice structure. | 2 |
| Figure 1.2 | Industrial applications of SiC. | 5 |
| Figure 1.3 | Applications of CMC in various fields of applications | 11 |
| Figure 1.4 | Powder pressing flow chart. | 14 |
| Figure 1.5 | Cold isostatic pressing | 15 |
| Figure 1.6 | Flow chart of SiC reaction sintering | 18 |
| Figure 1.7 | Flow chart of SiC PIP process. | 21 |
| Figure 1.8 | ExOne 3D printers | 24 |
| Figure 1.9 | Scheme of variable parameters involved during the SLS process. | 25 |
| Figure 1.10 | Advances in DLP and similar vat polymerization technologies: (a) multi-vat system for switching photopolymers for multi-material printing. (b) Multi-material printing with hybrid printing technology using DLP and DIW. (c) Schematic of CLIP method. (d) Schematic of HARP method. (e) Vat polymerization-based volumetric additive manufacturing. (f) Two-photon polymerization. | 27 |
| Figure 2.1 | Binary Ni-Si phase diagram. | 34 |
| Figure 2.2 | Ternary Ni-C-Si phase diagram at 1173K. | 35 |
| Figure 2.3 | Two different size SiC raw particles, a) XRD pattern; b) SEM image of large SiC; c) SEM image of small SiC. | 37 |
| Figure 2.4 | Thermal processing of SiC pellets: a) pre-sintering b) Infiltration sintering. | 38 |
| Figure 2.5 | Relative density curve of ideal PIP model and the real SiC samples, PIPed with pyrolysis at 1200 °C. | 44 |
Figure 2.6 (a) Overall porosity (solid line) and bulk density (dash line) of pyrolyzed samples (infiltrated with pure AHPCS or Ni-AHPCS mixture) vs PIP cycles, (b) a decrease in the fraction of open porosity removed in an infiltration cycle with increasing number of PIP cycles. ................................................................. 46

Figure 2.7 Microstructure of pyrolyzed SiC sample at 1200 °C: a) low magnification image of the section, b) higher magnification of a dense region, c) higher magnification of a porous region. ............................................................................................................. 47

Figure 2.8 Microstructure of SiC samples infiltrated with Ni nanoparticles and AHCPS: a)~b) at 1200 °C; c)~d) at 1275 °C. .......................................................................................................................... 49

Figure 2.9 XRD pattern of SiC samples (after 7 PIP cycles) infiltrated with pure AHPCS or Ni particle - AHPCS mixture and then pyrolyzed at 1200 or 1275 °C. a) long scan range; b) short scan range.......................................................................................................................... 51

Figure 2.10 Schematic diagram of SiC infiltration mechanism........................................ 52

Figure 3.1 (a)Lattice structure of the metal (dark gray circles) and carbon (light gray circles) occupies octahedral sites in Ni₃C; (b) Phase diagram of Ni-C system. .............................................. 55

Figure 3.2 Suggested growth mechanism of Ni₃C NPs in liquid phase reaction.............. 57

Figure 3.3 (a) Density vs PIP cycles of SiC pellets with additional Ni and carbon in polymer infiltration. (b) a change in the rate of porosity elimination with increasing number of a PIP cycle. ................................................................. 59

Figure 3.4 XRD pattern of SiC pellets with Ni and C addition after different PIP cycles (1275 °C). a) long scan range; b) short scan range................................................................. 60

Figure 3.5 Microstructure of SiC sample treated with Ni-AHPCS for the 1ˢᵗ-4ᵗʰ PIP cycles and with C-AHPCS for the 5ᵗʰ-7ᵗʰ after pyrolyzed at a, b) 1200 °C and c, d) 1275 °C.............. 61
Figure 3.6 XRD pattern of AHPCS-derived-SiC mixed with additional Ni and carbon nanoparticles after multi-cycle heat treatment (1200 °C).

Figure 4.1 A schematic showing printing defects between two spread layers and the effect of PIP and resulting gas cracks.

Figure 4.2 Die designs of regular and pressureless SPS: a) pressureless form of SPS using T-shaped punches, b) regular SPS subjected to applied external pressure, and c) another form of pressureless SPS with an additional graphite piece.

Figure 4.3 (a) Effect of pressure on the temperature needed to get 95% relative density for cubic ZrO₂. The corresponding decrease in grain size is also shown. (b) The effect of applied pressure on the density and grain size of cubic ZrO₂. Constant temperature of 1200 °C, hold time 5 min, heating rate 200 °C/min.

Figure 4.4 The exclude volume model of polymer infiltration and pyrolysis.

Figure 4.5 The μCT workflow applied in this work.

Figure 4.6 Density vs PIP cycle of pressed pellet and BJP SiC @1200 °C.

Figure 4.7 Cross-section SEM images of SiC after 7 PIP cycles (pyrolysis temperature – 1200 °C): a) pressed SiC, b) BJP SiC.

Figure 4.8 a) Density (solid lines) and open porosity (dash lines) vs PIP cycle curve of Ni effect on BJP3D and pressed SiC bulk, b) a decrease in the fraction of open porosity removed in an infiltration cycle with increasing number of PIP cycles.

Figure 4.9 SEM microstructure of SiC BJP bulk after 7 cycles PIP @1200 °C with: a) AHPCS and b) Ni-AHPCS.

Figure 4.10 CT-scanned, thresholded XY cross-sectional image for PIPed samples. White pixels indicate solid phases and black pixels indicate porosity.
Figure 4.11 Pore fraction plot of different SiC samples obtained from Z-stack images. ..... 85

Figure 4.12 Density vs PIP cycle on Ni nanaoparticle – AHPCS BJP SiC using different pyrolysis temperatures. ......................................................................................................................... 87

Figure 4.13 Density and close porosity vs PIP cycle curves of SPS applied BJP-SiC bulk samples........................................................................................................................................ 90

Figure 4.14 Microstructure of BJP-SiC samples after 1~4th PIP cycles with Ni addition and SPS process, (a)surface microstructure; (b) cross-section image of sample after SPS process; (c) after additional 5~7th PIP cycles with Ni addition................................................................. 91
List of Tables

Table 1 Mechanical properties of 6H(α)-SiC ................................................................. 3
Table 2 Popular sintering techniques of SiC and their presented relative density........... 29
Table 3 SPS and PIP method on BJP-SiC green body...................................................... 89
Chapter 1 Introduction

1.1 SiC Ceramics: Material Properties And Applications.

1.1.1 Crystal Structure And Mechanical Properties of SiC

Silicon carbide (SiC) is a semiconductor containing silicon and carbon. It occurs in nature as the extremely rare mineral moissanite. Since 1893, synthetic SiC powder has been mass-produced for use as an abrasive. Sintering of SiC powder produces very hard SiC ceramics that are widely used in various structural applications [1~3],

Crystal structure and properties of SiC have been well studied. A basic structural unit of SiC is a tetrahedron in the form of either SiC$_4$ or CSi$_4$. Four bonds of the tetrahedron have a nearly covalent character. An ionic contribution to the bond, which is calculated from a difference in electronegativity of Si and C is only 12%. Such a small ionic contribution to the interatomic bonds can also be deduced experimentally from the shift of the Kα doublet in the X-ray emission spectrum of Si in SiC [4].

The most remarkable feature of SiC crystal structure is its polytypism. The crystal structure of SiC has a number of different one-dimensional ordering sequences without any variation in stoichiometry. Although a great variety of SiC polytypes is known, it has become accepted practice to refer to the cubic polytype as β - SiC, and to all non-cubic structures (hexagonal and rhombohedral) collectively as α - SiC [5].
SiC crystals appear in a number of modifications that have either hexagonal or trigonal symmetry. They can all be described in the usual hexagonal axis system, with one c-axis perpendicular to three equivalent axes a, b, and d having angles 120° with one another. Previous study show that all crystallographic modifications of SiC have in fact very similar structures [5,6]: they all consist of identical layers perpendicular to the hexagonal or trigonal axes. In the direction of these axes, however, each structure has its own repetition distance, resulting from a characteristic variation of the stacking of the identical layers. The SiC₄ or CSi₄ tetrahedra are arranged in such a way that all atoms lie in parallel planes on the nodes of regular hexagonal networks, as presented in Fig. 1. The distances from the carbon plane to the neighboring silicon planes have a ratio 1:3 in relation to carbon-carbon interplanar distance.

Figure 1.1 SiC lattice structure [5].
Carbon - silicon bonds in the SiC₄ tetrahedra are very strong, which makes SiC very hard and chemically strong material. Silicon carbide is not attacked by any acids or alkalis or molten salts up to 800°C. In air, SiC forms a protective silicon oxide layer at 1200°C and is able to be used up to 1600°C. The high thermal conductivity coupled with low thermal expansion and high strength give this material exceptional thermal shock resistant qualities [7]. Silicon carbide ceramics with little or no grain boundary impurities maintain their strength to very high temperatures, approaching 1600°C with no strength loss. In addition, chemical purity, resistance to chemical attack at temperature, and strength retention at high temperatures has made this material very popular as wafer tray supports and paddles in semiconductor furnaces.

Table 1 Mechanical properties of 6H(α)-SiC [6]

<table>
<thead>
<tr>
<th>Properties</th>
<th>SiC (in Wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density g/cm³</td>
<td>3.2</td>
</tr>
<tr>
<td>Compressive Strength (MPa)</td>
<td>1395</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>240</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>2200</td>
</tr>
<tr>
<td>Hardness (Moh’s scale)</td>
<td>9-9.5</td>
</tr>
<tr>
<td>Fracture toughness(MPa-m⁷)</td>
<td>4.6</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>Hexagonal</td>
</tr>
</tbody>
</table>

Silicon carbide is a commonly used wide-bandgap semiconductor (2.0eV<Eg<7.0eV), well-suited for high temperature operation. While most traditional integrated circuit technologies
using silicon devices are not able to operate at temperature over 250°C, SiC based devices for high-temperature circuit operation from 350°C to 500°C is desired for use in aerospace application, nuclear power instrumentation, satellite, space exploration and geothermal wells [41~46]. Owing to the much wider energy bandgap of a 4H-SiC material compared with Si, its intrinsic carrier density is much smaller, which enables a high-temperature operation capability from a blocking stability point of view. The ideal specific conduction resistance (Ron,sp) of a SiC unipolar device can be much smaller than that of its Si counterpart. The smaller Ron,sp enables SiC chips to be smaller, leading to lower parasitic capacitance and higher switching speed. As a result, it is possible to achieve both low switching loss and low conduction loss for a wide range of blocking voltages and frequencies. Generally, SiC power devices will enable further rapid evolution of power electronics systems toward even higher efficiency and power density. In addition to high-temperature applications, SiC has potential for use in high power, high frequency and high radiation resistance environments [47~49].

Silicon carbide ceramics are essentially in a variety of industries due to their unique combination of properties, such as excellent mechanical strength, good chemical resistance, high thermal conductivity, low thermal expansion coefficient, and high thermal shock resistance. This popular non-oxide ceramic has long been acting as both matrix and reinforcement, usually finding its applications in silicon-based CMCs such as engines of rockets and automobile, pistons and bearing, turbine disks, electronic devices like LEDs, artificial teeth, and other industrial applications.
1.1.2 Application of Mechanical Properties of SiC

Aerospace. SiC-ceramic matrix composites (CMCs) are potential material candidates for the fabrication of hot structures of spacecraft. Here, the maximum temperature ranges from 800 to 1600 °C, during the ascent and re-entry phases of a flight, the structures being submitted to thermal shocks and cyclic mechanical loading under ablative or passive oxidizing atmospheres, with an expected durability of a few tens of hours. Such conditions are compatible with modern composites fabricated with carbon fibers and engineered multi-layered self-healing matrix. Moreover, such materials approach will benefit from the high refractoriness of C/SiC composites (up to 2500 °C) relative to the low melting point of aluminum (650 °C) in metallic option.
combined with a thermal insulation. Similar materials could also be used for the shielding of satellites against the impact of meteorites or foreign objects owing to the high toughness and hardness of these materials [9].

**Automotive.** Another field of application is that of the hot structures of Aerojet engines and related gas turbines, which are presently made of heavy, low melting point nickel-based superalloys that require complex cooling systems. Replacing superalloys by SiC-based composites would permit to raise the gas temperature, suppress, or limit the cooling requirement, increase the efficiency of the engine, and reduce both the weight and the noise/pollution level. E.g., the combustors and the afterburner parts such as the flaps of the exhaust nozzles. The outer (divergent) flaps of exhaust nozzles experience a temperature that is relatively low (T<700°C). Hence, they can be fabricated with carbon fiber-reinforced SiC-matrix, with a weight gain of 50%. The inner (convergent) flaps of the exhaust nozzles are exposed to higher temperatures (up to 1100°C). Durability of the order of 1000 h has been demonstrated for 3D-composites with a self-healing multilayered matrix based on bench combustion tests. Large combustors of a concentric cylindrical liners have been fabricated using SiC (Hi-Nicalon)/BN/SiC (Si) ceramics matrix composites (CMC) made by chemical vapor infiltration (CVI) or reactive melt infiltration (RMI) methods. Durability of several 10,000 h has been established under real service conditions, for composites with a BSAS–environmental barrier coating (EBC) [8,9].

**Industrial.** The braking system is another field of applications for SiC ceramics. Aircraft and racing car disk brakes are fabricated with carbon fiber reinforce SiC (C-SiC) composites sliding against themselves. In comparison to relative to conventional steel disk brakes, C-SiC brakes display a lower density, a higher service temperature (and hence improved security), good friction properties at high temperature, and longer lifetime. Due to their good friction and wear
resistance near ambient temperature and in wet atmosphere, C-SiC receives more attraction. SiC matrix is formed by a combination of carbon-PIP and SiC (Si)-RMI techniques [9]. Coated C-SiC (Si) brake disks, sliding against themselves or pads (organic or metallic), show a higher coefficient of friction less depending on moisture and a very low wear. They are now proposed as an option for cars and could be extended to other fields (trains, lifts, etc.).

**Medical.** SiC-based ceramics are also good materials in medical applications. The laminated SiC-based ceramics (TiSi$_2$ and Ti$_3$SiC$_2$) ceramics are great instances of biologically produced substances and materials because they have the adaptability to give particular anisotropy qualities such as strength properties, durability, and stiffness, as well as impact and damaging resistance [61]. Due to its optical characteristics, dental ceramics resemble real teeth in appearance. Other material properties such as high strength and chemical resistance, allowed these materials to be manufactured promptly for dental applications. A zirconia infiltrated with silica gel improves in two directions such as structural uniformity and resin cemented adhesion. This type of infiltration procedure is straightforward to carry out and control in a prosthetic laboratory [62]. They have essential properties such as chemical stability and inertness, low toxicity, biocompatibility which are important to medicinal and its industrial applications [63].

**Nuclear.** SiC-matrix composites might become key structural materials in high temperature nuclear reactors of the future, based on their refractoriness, HT-mechanical properties, high thermal conductivity, and more importantly low activation under radiation. The main concerns being: the combined effect of temperature and radiation on the structure and mechanical properties of both SiC fiber and matrix, the nature of the interphase (thick layers of carbon or BN being inappropriate under radiation), the effect of activable impurities in the
composites, the thermal conductivity, and the corrosion by residual or in situ formed gaseous species.

_Military._ Carbon fiber coupled with ZrC-SiC composites is recommended for high temperature applications including supersonic aircrafts and sharper surfaces in aircrafts. These composites have excellent features such as fracture toughness, thermal shock absorption, and possess good mechanical characteristics under higher temperatures [67,68]. Composites like C/C-SiC and SiC/SiC are extensively used as functional materials in the aviation industrial sectors due to their higher thermal prevention, enhanced propulsive systems, and other properties such as higher fracture toughness, strength at higher temperatures, reduced density, superior thermal conduction, and oxidative resistance [69,70].

1.1.3 Application of Electrical Properties of SiC:

In addition to excellent mechanical properties, SiC exhibits intriguing electric properties that are suitable for the application of wide band gap semiconductor devices. A revolutionary development in recent entry years has been the introduction of power devices of WBG materials such as SiC, as a WBG material, SiC has the advantage on electronic devices with low on-resistance electric current, high operation voltage window, high melting point, high breakdown field, more saturation velocity, also high temperature resistance and thermal conductivity in comparison with Si-based devices.

_SiC solar inverter._ In the past decade, the solar inverter has progressed toward higher efficiency, higher density, and lower cost. SiC devices have been investigated in different types of solar inverters. For rooftop applications, a desirable weight density is necessary, e.g., 1 kW/kg. Most commercialized products with Si insulated-gate bipolar transistor (IGBTs) cannot
fulfill this requirement; their weight density is less than 0.38 kW/kg. To address this challenge, people present a 50-kW SiC metal-oxide-semiconductor field-effect-transistor (MOSFET)-based photovoltaic string inverter with significantly increased switching frequency and reduced weight, which achieves the design target. High-power centralized inverters based on SiC devices have also been developed. A 1 MW solar converter system consisting of a boost converter with an all-SiC power module and a Si-based three-level, T-type, neutral point-clamped structure is presented [8].

*Electrical vehicle.* SiC devices are enablers for high power density, which is the most important requirement for power electronics circuits in EVs, almost comparable in importance to cost. By designing a SiC powder device, EVs can achieve 35% reduction in size and 40% reduction in weight and loss [23]. As the cost of these devices drops, more and more EV manufacturers will be using SiC devices. The power electronics circuits in electric drive systems typically include a boost dc–dc converter (currently used in hybrid EVs) that increases the battery voltage (up to 700 V), a traction inverter, a DC - DC converter for auxiliary loads (high-voltage bus to 14 and 42 V conversion), and an onboard charger (OBC).

1) The boost DC - DC converter requires higher voltage-rated devices (1.2 kV) that can run at high frequencies in the tens of kHz, e.g., a 20 kW buck/boost converter running at 100 kHz. The ideal device for this application today would be based on wide band gap semiconductors like SiC. Running at high frequencies allows the filter components to be much smaller, resulting in higher power density. To achieve these high frequencies, power device packages must be designed with minimum parasitic inductance on the order of less than 10 nH.
2) The traction inverter does not need higher switching operation, but lower loss switching and conduction will result in lower losses and less need for thermal management. SiC-based devices rated at 900 and 1200 V are ideal as traction inverter power devices.

3) Present-day OBCs are designed for wired operation, but future versions will have wired and wireless options or both. Typical OBCs will require high frequency switching devices [24~26].

Since SiC devices are much smaller than their Si counterparts, it is difficult to reliably package them and cool them as needed. In electric drivetrain technology, the trend is toward double-sided packaging, to eliminate wire bond, enhance cooling efficiency, and reduce parasitic inductances.

**Induction heating.** Inductor heating (IH) is a relevant example of a technology that is boosting its performance and application range by using SiC devices. Resonant power converters usually operate at 10 kHz to the 1 MHz range, and the power range varies from 1 kW in domestic and medical applications to several MW in industrial applications. These designs imply challenges regarding blocking voltages, switching losses, and operation in harsh environments that perfectly match the features of SiC devices, opening the design window to high performance converters and innovative IH applications [39,40].

**High-voltage SiC devices:** High-voltage SiC devices provide significantly higher voltage–frequency capability, which enables medium-voltage and high-frequency power conversion. Compared with traditional transformers with same rating, it has a 50% reduction in size and 75% reduction in weight, while achieving 98% of efficiency. Another potential
application of high-voltage SiC devices is the circuit breaker. The SiC ETO has been applied to both circuit breakers and hybrid circuit breakers for the medium-voltage grid [64].

![Applications of CMC in various fields of applications](image)

**Figure 1.3** Applications of CMC in various fields of applications [62].

### 1.2 Processing of SiC Ceramics.

#### 1.2.1 Traditional Sintering Process of SiC

Silicon carbide (SiC) is one of the most interesting ceramic materials due to its superior properties. However, the strong Si-C covalent bonds make it difficult to produce fully dense SiC without aids like sintering additives or external pressure. In early development of sintering
techniques, high temperature solid-state sintering and liquid-state sintering have been studied for long period.

**Solid-state sintering:** Pressure-less sintering of SiC was first reported by Prochazka via solid state sintering mechanism by using boron and carbon as aids [50]. It was shown that one effect of boron was to promotes densification by segregating at the grain boundaries, thus reducing the grain boundary energy, preserving short diffusion distances and a higher density of matter sources (grain boundaries formed at contact necks) which would quicken densification process, whereas the role of C is to increase the surface energy of SiC by removing the native SiO$_2$ film via a carbothermal reduction process [51]. Although this process is the most diffuse technology to manufacture ceramic components, sintering temperature over 2100 °C is still required in order to obtain high density products [52,53]. Such high sintering temperature would result in a higher cost of SiC products, and also cause an increased grain growth which can compromise the mechanical properties.

Processing temperature of solid-state sintering can be decreased by hot press sintering (also called hot isostatic pressing, HIP). With this technique, Chen et al. [8] produced high toughened SiC ceramics using aluminum, boron and carbon as additives. HIP of Al$_2$O$_3$-doped SiC had an ultra-fine-grained microstructure with grain size varying from 0.5 to 2.5 mm [10]. High density and small grain size of HIP samples exhibit good mechanical properties and workability. HIP method combines pressing and sintering, causing consolidation of powder particles, healing voids and pores. The pressure medium of HIP is nitrogen or argon gas. The working pressures, which are applied in the hot isostatic pressing method, are commonly between 15,000 psi to 44,000 psi (100 MPa to 300 MPa). The part shrinks and densifies, forming high strength structure. E.g., cans made of stainless steel, or mild steel are used in the HIP
method. In HIP, the main advantage is the great flexibility in sample shapes. The method may be used without mold. In this case the part is first compacted by cold isostatic pressing method, and then it is sintered in order to close the interconnecting porosity. The sintered (but still porous) part is then pressed isostatically at high temperature without any mold. In HIP, pre-sintered silicon carbide ceramics with low density were densified by HIP under 200 MPa in a nitrogen atmosphere in 1850 °C. It was confirmed that surface defects were healed and open pores became closed. The relative density increased from 90.6 to 98.5%. The room temperature bending strength increased by 82.3% and the fracture toughness was enhanced up to 8.4 MPa.m$^{1/2}$ [10].

A more commonly used SiC densification process is combining powder pressing and sintering. Prior to shape forming, ceramic materials are mixed with additives like binders, plasticizers or water. The popular pressing techniques including uniaxial (die) pressing and isostatic pressing. Die pressing is the powder compaction method involving uniaxial pressure applied to the powder placed in a die between two rigid punches. This method is effectively used for mass production of simple geometry parts. The pressing process consists of following stages: a) Die filling; b) Compaction; c) Green compact part ejection; d) Removal steps (Figure 1.3).
Isostatic pressing is the powder compaction method involving applying pressure from multiple directions through a liquid or gaseous medium surrounding the compacted part. Cold isostatic pressing (CIP) is conducted at room temperature. A flexible (commonly polyurethane) mold immersed in a pressurized liquid medium (commonly water) is used in the cold isostatic pressing method (Figure 1.4). There are two types of cold isostatic pressing: wet bag and dry bag. In the wet bag method, the mold is removed and refilled after each pressure cycle. This method is suitable for compaction of large and complicated parts. In the dry bag method, the mold is an integral part of the vessel. The dry bag method is used for compaction of simpler and
smaller parts. Cold isostatic pressing has the advantages of producing better uniformity and more complex forms of compact.

![Cold isostatic pressing diagram](image)

**Figure 1.5** Cold isostatic pressing [10].

Once the green body is prepared, SiC green bodies needs to be sintered at high temperature. A problem of SiC is strong covalent Si-C bonding which enables the densification of SiC green bodies at extremely high temperature (>2000 °C). To reduce the sintering temperature, liquid phase sintering was developed as an alternative pressure-less sintering technique.

*liquid phase sintering*: Doping of impurities is a well-known method. For example, dopants such as B and C can control bulk and surface diffusion of atoms during solid-state sintering, while oxide dopants such as Al₂O₃ and Y₂O₃ are reported to form a liquid phase and enhance the densification of SiC ceramics. Appearance of a liquid phase is due to the formation of a eutectic melt between oxide dopants and SiO₂ that is intentionally or unintentionally added to SiC during the powder synthesis and high-temperature sintering processes.
Liquid phase sintering can be controlled by following factors, including: 1) The specific surface area of SiC powder; 2) The sintering atmosphere (Vacuum, N₂ or Ar); 3) The amount and composition of liquid phase; 4) The use of a powder bed, sintering time and temperature, and also include the processing methods used prior to firing. The usual ratio of additives Al₂O₃ and Y₂O₃ are Al:Y>1 and total additives weight ratio is 5%~15% of SiC [52]. The higher ratio of sintering additives, the higher sintering rate, but meanwhile lower the mechanical properties and product purity [53]. Some other replacement additives instead of Al+Y oxide including: Mg+Al oxide; other rare earth element+ Al₂O₃; Y+Al nitride; only Al₂O₃ [54~58].

The sintering temperature of liquid phase method is lower than solid-state sintering, but not much. Based on different sintering atmosphere, the sintering temperature in Ar is ~1900 °C and sintering temperature in N₂ is ~2100 °C. The effect of atmosphere also results in a little more weight loss upon sintering at N₂ than Ar, meanwhile grain growth is a little higher in N₂ than Ar.

It was reported that people can use powder beds and close containers to reduce the weight loss of sintered SiC [59,60]. The effect of specific surface area was also observed to have a positive relation with sintering rate, as the SiC powder with specific surface area 10~15 m²g⁻¹ showed higher sintering rate than SiC powder with specific surface area ~5 m²g⁻¹[65].

Compared with solid-state sintering of SiC with additives like B and C, liquid phase sintering has a higher strength which is twice as high [56~58]. This higher strength is related to the much higher fracture toughness and a change from transcrystalline to intracrystalline fracture behavior [58~60]. Meanwhile, the hardness of LP-SiC is similar to solid-state sintering with B and C.
1.2.2 Reaction Sintering

The so-called reaction sintering is a chemical reaction, which takes place at the interface of a porous blank and a gas phase or liquid phase. Therefore, the mass of blanks will be increased and the number and size of small openings will be reduced. Hence, the blank is sintered into a finished product with high strength and precision. As compared with other sintering technology, reaction sintering has advantages such as small changes in part dimensions and compaction in part density. Thus, this method can be used to manufacture parts of accurate dimensions. In the reaction sintering of SiC, the processing temperature is decreased below 1500 °C and a fully dense structure can be obtained. Furthermore, it has good shape capability for large and complex shape parts, because the dimensional changes are almost negligible during the process.

Liquid Silicon Infiltration (LSI) technique is a popular type of reactive melt infiltration (RMI) technique, in which the ceramic matrix develops as a result of chemical relationship between the molten material infiltrated into a porous reinforcement phase preform and the substance surrounding the melt, which can be solid or gaseous.
In a typical reaction sintering process of SiC matrix composite, the green body comprises only graphite particles or a mixture of graphite particles and SiC particles. The green body is formed first by cold pressing and is machined to have a specific product shape. Then, the machined green body is infiltrated with liquid phase silicon above the melting temperature of Si (1410 °C). Chemical reaction takes place between the melted silicon and carbon to produce SiC which may be bonded to SiC grains existing in the green body. Since infiltrated silicon is not completely reacted and remains in the sintered body. The final parts from the reaction sintering contain 8 - 10% silicon and 90 - 92% of SiC [11]. Because of the residual silicon, the mechanical properties, such as strength, Young’s modulus, fracture toughness and hardness of the reaction-sintered SiC are lower than these of the normally sintered SiC [11].
The melt infiltration (MI) process is an alternative route, also called liquid silicon infiltration (LSI). This process is widely used to make composite material from the ceramic preform with porosities. The molten silicon wets the carbon preforms surface and the capillary pressure help the melt seep into the porous material. The wetting conditions between the solid ceramic and liquid metals are important for performing the MI process. During the phase of infiltration, the weight of the final composite can be monitored. It can be measured before consolidation as well as through the process of this infiltration [64].

1.2.3 Polymer Infiltration

SiC ceramic composites may be produced by traditional ceramic fabrication methods including mixing the powdered matrix material with the reinforcing phase followed by processing at elevated temperature: hot pressing, sintering. Such fabrication routes are successfully employed for preparing composites reinforced with a discontinuous phase (particulate or short fibers). However, the composites reinforced with continuous or long fibers are rarely fabricated by conventional sintering methods due to mechanical damage of the fibers and their degradation caused by chemical reactions between the fiber and matrix materials at high sintering temperature. However, SiC ceramic composites reinforced with long fibers are commonly fabricated by infiltration methods.

Polymer infiltration and pyrolysis (PIP) is a chemical processing which requires lower average processing temperatures, with more effective atomic mixing of composite components and hence greater homogeneity. In this method, a liquid precursor form of the ceramic is infiltrated into the low dense green body of matrix phase. The precursor is then converted
typically by thermal decomposition in the polymer precursor process. The resulting matrix consist of initial raw material and converted amorphous phase, which must be more densified and then the process repeated several times to form relatively high dense matrix [12]. The PIP process of a SiC CMC consists of following steps:

1) Prepreg fabrication: Pre-process of SiC raw materials such as SiC fibers with resin binder (e.g., PEG). After mixing, prepgress may be dried or partially dried. In such plastic condition the prepgress can be laid up to shape the desired architecture.

2) Shaping: The prepg is laid up on a mold or other shaping tools and followed with a molding process (pressure-less shaping or compression molding). After the molding, a weak and brittle SiC green body is formed.

3) Pre-sintering: SiC green body is very weak and brittle which cannot keep its geometric shape during polymer infiltration, so a pre-sintering process is introduced to solidify the SiC green body and remove polymer binder. This process requires higher temperature than pyrolysis (1500 °C).

4) Polymer infiltration: The cured SiC shape is immersed into a low viscosity solution of a preceramic polymer, which infiltrates the porous structure and filling the spaces between SiC particles. The infiltration process is driven by the capillary force but vacuum assist will increase the efficiency.

5) Pyrolysis: Pyrolysis is the chemical decomposition of polymers by heat in the absence of oxygen. The preceramic polymer in this study is AHPCS which decompose into amorphous SiC and other gaseous residue under 1200 °C. The chemical decomposition of polymer precursors results in a release of volatile products such as CO, H₂, CO₂, CH₄, and H₂O. The
ceramic material obtained in the pyrolysis of a polymer has a porous structure due to the shrinkage caused by the release of the volatiles.

6) Multiple cycles of infiltration and pyrolysis: A PIP cycle is repeated 5 - 7 times to increase the density of SiC composites.

![Flow chart of SiC PIP process.](image)

**Figure 1.7** Flow chart of SiC PIP process.

In comparison to traditional solid-state or liquid-phase sintering, the PIP technique of SiC ceramics has several advantages: 1) The ceramic matrices are formed at relatively low temperature. 2) Good control of the ceramic matrix microstructure and composition. 3) Different types of raw material can be used (different size of particles and fibers). 4) Wide range of
matrices may be fabricated (Based on shaping technique). 5) No free silicon in the matrices (Compared with traditional reaction sintering process).

Though PIP method is a powerful way to manufacture SiC ceramics, traditional PIP method has several disadvantages: 1) Long fabrication time as a cost of multiple PIP cycles. 2) Low converted rate of preceramic polymer makes it high cost in producing dense SiC composites. 3) The residual porosity present in the matrix microstructure affects the mechanical properties of the composite.

To achieve reasonable matrix densities, three general parameters must be optimized:

1) Quality of preceramic precursor - high ceramic yielding, phase and chemical purity upon pyrolysis, and controlled microstructure evolution.

2) Porosity of green body before the infiltration step - minimal and completely open porosity in green body compacts and during each PIP cycling.

3) Microstructure of final composites - controlled densification with minimal grain growth of SiC grains during sintering.

1.3 Additive Manufacturing of Ceramics

The development of additive manufacturing (AM) technology makes it easier to fabricate complex-shaped and high accuracy components. In previously reported AM fabricated SiC, low density and low mechanical strength always limits the application of 3D printing SiC composite. Among these reported AM technologies, selective laser sintering (SLS), which fabricates the
parts via employing a carbon dioxide laser beam to sinter the powder materials selectively, exhibits the best potential in fabricating the ceramic components.

1.3.1 Binder-jet Printing

Traditionally, monolithic SiC is made by powder processing techniques (such as pressing), which in most cases are restricted to the fabrication of objects with simple shapes. However, additive manufacturing (AM) has demonstrated the potential of revolutionizing the manufacturing of ceramics, including SiC by the ability of manufacturing objects with complex shapes, without having to involve expensive machining operations. Among the various AM methods that currently available for shaping ceramic powders, binder-jet 3D printing (BJ3DP) is the most popular one because it has highest efficiency (compared to other AM methods) while maintaining high spatial resolution.

Binder jet printing (BJP) is an additive manufacturing process where structural materials in the form of powder, also called fillers, is connected with the help of binder or printing liquid deposited by a print head. An Innovent binder jet system from ExOne Company was used for 3D printing. After printing, the powder bed goes under a binder curing step (200°C, 6 hours) that drives off the majority of organic-based binder.

The printed part can then be subjected to post processing to achieve fully dense using methods such as PIP, CVI or RMI. BJP can be used to manufacture parts made with a wide range of materials including metals, ceramics and polymers. Plenty of advances in BJP are making it a viable option for facile manufacturing of ceramic parts with complex geometry, due to faster manufacturing time and low cost [13]. However, this application is limited by the high volume of pores and consequent low density due to the limited packing factor of powder materials.
Moreover, high volume shrinkage is observed during post-processing resulting in dimensional inaccuracy and creep formation. The presence of porosity makes the printed parts brittle and has a negative effect on mechanical properties.

![ExOne 3D printers](image)

**Figure 1.8** ExOne 3D printers [16]

1.3.2 Selective Laser Sintering (SLS)

Selective laser sintering is an interesting application on dry silicon carbide-silicon powders beds. It was originally developed at the University of Texas at Austin and commercialized by DTM Corporation between 1987 and 1992 [71]. The SLS process utilizes a laser beam to fuse powder particles together to form a solid layer representing a numerically defined cross-section of a prior generated CAD model. By depositing new layers of powder and repeating the laser scanning process, a solid representation of the CAD model is generated layer by layer. SLS parts are particularly adept for tooling and end use components due to their good achievable mechanical strengths.
In the SLS process of SiC matrix composites, silicon is used as binding phase for the SiC powders. It is further converted by reaction bonding into silicon carbide by providing extra carbon to the powder system. This technique has both advantages and disadvantages. Among the advantages, SLS is easy to use and can be applied on industrial manufacturing. Disadvantages of SLS include low accuracy in printing the complex architecture and restriction on particle size of raw materials [14].

1.3.3 Digital Light Processing

Digital light processing (DLP) is an attractive AM technique using photocurable resins as basic materials. It can be used to fabricate a single layer of the 3D object through spatially controlled solidification by using a projector light (either UV or white light), to form a layer rapidly. Also, it is possible to tailor the final properties of the printed object by simply changing

Figure 1.9 Scheme of variable parameters involved during the SLS process [14].
the photocurable resin formulations. By doing so, it is possible to achieve a large variety of systems to produce structures with advanced properties and functions. The ceramic suspensions were commonly prepared by mixing ceramic powders and acrylate resins for 3D printing. However, only a limited amount of particles (~50%) can be mixed into photosensitive resin to form homogeneous and stable suspensions. Furthermore, some ceramic powders with high refractive index exhibit high light refraction and absorption, which significantly reduces the light penetration depth in the suspension and disables DLP printing process. Currently, DLP printable photocurable resin containing CNT fillers or in situ generated silver nanoparticles with enhanced electrical properties have been developed to 3D printing conductive structures [15].
Figure 1.10 Advances in DLP and similar vat polymerization technologies: (a) multi-vat system for switching photopolymers for multi-material printing. (b) Multi-material printing with hybrid printing technology using DLP and DIW. (c) Schematic of CLIP method. (d) Schematic of HARP method. (e) Vat polymerization-based volumetric additive manufacturing. (f) Two-photon polymerization. [85]
1.4 Challenges of SiC Sintering Technique and Current Problems of AM Technique

Traditional solid-state sintering of SiC ceramics requires very high sintering temperature (2100 °C) or pneumatic pressure loading. To address manufacturing problems of SiC, people developed liquid phase sintering and added sintering aids which lower the sintering temperature to ~1800 °C, for further improvement of sintering process, relatively new techniques such as the reaction sintering and PIP have been developed. However, these techniques also have their following issues.

Reaction sintering is a relatively low-temperature process with a capacity of good shape capability and low cost. The main disadvantage of this technique is remaining Si in the final SiC matrix. Due to the partial reaction between Si and C, reaction sintered SiC ceramics contain approximately 10 - 40% of residual Si in the matrix. This, in turn, decreases the mechanical strength of SiC at high temperature where melted Si becomes viscous.

Normal PIP method is an alternative manufacturing technique which lowers sintering temperature down to <1200 °C and does not leave the liquid phase in SiC matrix. However, the solid loading of SiC ceramics seldom reach >90 % even if PIP cycles are repeated multiple times. The porosity of SiC ceramics from the PIP method is normally around 10%. The high porosity of final products is attributed to the clogging of pore channels during the pyrolysis steps when polymer precursor decomposed into amorphous SiC.
<table>
<thead>
<tr>
<th>Table 2</th>
<th>Popular sintering techniques of SiC and their presented relative density [64].</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Solid-state sintering</strong></td>
<td>High purity and crystallinity, can reach high bulk density</td>
</tr>
<tr>
<td><strong>Liquid-state sintering</strong></td>
<td>Required lower temperature than solid state sintering (~1800°C), higher fracture toughness and hardness.</td>
</tr>
<tr>
<td><strong>Reaction sintering</strong></td>
<td>Sintering temperature is much lower than normal sintering (~1600°C), good shape capability, high purity because no additives, low cost.</td>
</tr>
<tr>
<td><strong>Polymer infiltration and pyrolysis</strong></td>
<td>Much lower sintering temperature required. (900–1200°C). Controllable density and microstructure by adjusting raw materials and packing method.</td>
</tr>
</tbody>
</table>
1.5 Hypothesis and Objective

Hypothesis

a) If SiC preceramic is mixed with metal nanoparticles and infiltrated into SiC matrix in the early PIP steps, the eutectic reaction occurs in the part of infiltrated material and the liquid phase of metal silicide forms at low temperature. The capillary force of the liquid phase prevents clogging of pore channels of SiC matrix and enhances the infiltration behavior of preceramics in subsequent PIP steps.

b) If SiC preceramic is mixed with carbon nanoparticles and infiltrated into SiC matrix containing residual metal silicide, the metal silicide can react with carbon nanoparticles and return to the carbide phase. Hence, sequential infiltration of the preceramic – metal nanoparticle mixture and the preceramic – carbon mixture during the PIP process enables the use of transient liquid phase and lead to the SiC ceramics of the low porosity and the small impurity amount.

c) The modified PIP process using the transient liquid phase can address the problems of binder jet processing of SiC ceramics, which include the high porosity of printed ceramics green body and the high sintering temperature of SiC powder. The infiltration steps can fill not only intergranular pores but also extended defects that are formed during the binder jet process.

Objective

The objective of this research is to improve the densification of SiC ceramics which are produced from PIP method, without leaving the second phase that can be viscosified near 1000 °C. A transient liquid phase is introduced by adding Ni nanoparticles into SiC preceramic and removed by adding carbon nanoparticles into SiC preceramic. Alternate infiltration of two
different preceramic polymers makes silicide melt transient, which is key to producing SiC ceramic with high density and excellent mechanical properties. To achieve the objective, a connection between each processing factor and sintering behavior of SiC ceramics will be explored systematically. The proposed method in this study will result in the high density due to the formation of a low melting point liquid silicide phase that facilitates reaction bonding followed by reabsorption of the liquid to reduce the silicide phase fraction in the final ceramics. A newly developed PIP method is also applied to AM shaped SiC green bodies such as the binder-jet printing. It is carefully examined how a difference in the porosity of SiC preforms (pressed and binder-jet printed green bodies) influences the infiltration of the SiC precursor – nanoparticle mixture and the densification of final SiC ceramics.
Chapter 2 Enhanced Densification in The Polymer Infiltration Process of SiC Using the Formation of Liquid Phase

2.1 Introduction

Traditional pressure-less sintering requires a very high temperature (1800~2000 °C) [11,13], which increases the cost of SiC sintering. To address this problem, different techniques such as reaction sintering and polymer infiltration and pyrolysis (PIP) were developed to reduce the sintering temperature to 1000~1400 °C. In addition, PIP process is more controllable in purity and density of SiC products [14,15]. Polycarbosilane (PCS), [SiH(CH3)CH2]n and allylhydridopolycarbosilane (AHPCS), [Si(CH2CH=CH2)2CH2]x[SiH2CH2]n−x, are two well-known preceramic polymers which are used to infiltrate into SiC preforms [17~19]. They are explored as matrix resin for SiC ceramics and have following characteristics: 1) since they are relative stable in air at room temperature and very stable in -10°C environment, they are easy to store; 2) they are liquid at room temperature and their low viscosity is suitable for the infiltration; 3) the products of the pyrolysis are relatively pure and the crystal structure of the final products depends on heat treatment temperature (β-SiC and some excess carbon from 1400°C treatment, amorphous-SiC from 1000 °C treatment).

The PIP method can be combined with shaping methods such as traditional powder pressing and additive manufacturing to produce SiC preforms of different geometries [17~22]. For example, preceramic polymer was mixed with SiC powders as the binder. The mixture was mechanically pressed at high pressure (250MPa) to shape the SiC green body. After sintering at 930 °C, the best relative density reached 77% of theoretical density [19]. PIP was also used in the densification of green bodies prepared by a stereolithography method. The photosensitive
SiC slurry was shaped into a green body under digital light stereolithography. PCS was used as the preceramic polymer for the PIP process and repeated up to 8 cycles. The highest relative density was 84.8%, though a complex shape remained stable during multi-cycle PIP process [19~21]. In most previous PIP studies, the density of SiC ceramics was in a range of 75 – 85% and the infiltration efficiency became low with increasing number of infiltration cycles. This fundamental limitation of the PIP method is explained by the blockage of open pores near the surface [22]. As the PIP cycles were repeated 5~6 times, open pores changed to closed pores even though the density of the sample is still around 80% that is considered as an intermediate sintering stage [22]. Therefore, preceramic polymer liquid cannot penetrate into the bulk of samples during the infiltration and there is no further increase in the density.

This section addresses the fundamental problem of the PIP which is the blockage of the pore channels during the intermediate sintering stage. In previous studies, some oxide nanoparticles (such as Al₂O₃ and Y₂O₃) have been used in sintering process to improve the bulk density [26]. The oxide additive component formed the lower melting point liquid phase during sintering process and had reaction with SiC to form Al₂O₃/Y₂O₃-doped SiC. This led to the decrease of bulk porosity but on the other hand large amount of additives also reduce the hardness of SiC bulk products [27].

Here, a more effective additive material, nickel nanoparticle (Ni NPs), is applied. Preceramic polymer was mixed with nickel nanoparticles so that nickel silicide would form during heating. Figure 2.1 shows the phase diagram of Ni-Si system. The reaction between SiC and Ni nanoparticles during high temperature annealing was established and a ternary phase diagram was also showed in Figure 2.2. It has been reported that Ni can react with Si in bulk diffusion pathway, in intermediate phases between contact surface are gradually changed from
low Ni:Si rate to high rate (NiSi/ Ni$_2$Si/ Ni$_5$Si$_2$). Contrary to binary system, the reaction pathway in Ni-Si-C ternary system is a more composition and temperature related result, reacted phases highly related to composition of Ni and Si, also the melting temperature of each intermediate phase will affect the type of carbide phases in the final composition. In this chapter, Ni amount is always in a minority state and low Ni:Si ratio phases (NiSi) will be prior to remaining after the high temperature processes.

Figure 2.1 Binary Ni-Si phase diagram. [72,73]
It was expected that Ni$_2$Si and NiSi phases would form a liquid phase at high temperature of the pyrolysis step, facilitate the redistribution of mass in the infiltrated material, and prevent open pores from being plugged. This helps to improve the infiltration efficiency. The sequential addition of nickel and carbon nanoparticles removes residual Ni$_2$Si and NiSi phases in the final products and removes the possibility of deterioration of the mechanical strength at high temperature. A relative density of SiC ceramics from this study reaches 92.2% (after 7 PIP cycles) and 93.2% (after 10 PIP cycles) which is much higher than that of SiC ceramics from traditional PIP.

**Figure 2.2** Ternary Ni-C-Si phase diagram at 1173K. [74,75]
2.2 Experiment

2.2.1. Sample Preparation

*SiC slurry preparation:*

SiC coarse powder (purity: 99.8%, 400 mesh size, Sigma Aldrich) and SiC fine powder (purity: 99.6%, average size: 0.9 μm, Saint Gobain) were used as raw materials. The raw material characterization results were shown in Figure 2.3, both have 6H-SiC crystal phase.

Two kinds of β-SiC particles (average size: 17 μm and 1.2 μm) were used as starting material. This combination helps to increase the packing density of green bodies after pressing. The packing density of spherical particles is expected to reach the highest value when two kinds of particles with a size ratio of large: small =10:1 are mixed [23]. β-SiC was chosen since it is stable in <1500 °C. A typical preparation process of SiC bulk sample is described below.

Green body shaping and pre-sintering: Coarse and fine β-SiC powders were mixed at a weight ratio of 3:1 using DI water with 3 wt% of polyethylene glycol (PEG) as binder. PEG was first dissolved in DI water and then SiC powders was added. The resulting slurry was then mixed in an ultrasonic bath and planetary mill and then dried at 80°C until only a small amount of water was left. Powder was then uniaxially pressed at 200~250 MPa. Pressed pellets were presintered in a carbon crucible at 1500°C for 2 hours under vacuum.
Uniaxial pressing method was applied to shape the SiC powder, a pressing mold was used to hold the SiC powder and an oil-pressing machine was used to shape the green body. For each sample pellet, 0.5g powder was used and pressure was controlled at 250~300Mpa. The obtained pellets were placed in a carbon crucible and then put into a vacuum furnace to pre-

Figure 2.3 Two different size SiC raw particles, a) XRD pattern; b) SEM image of large SiC; c) SEM image of small SiC.

**SiC green body pre-sintering:**

Uniaxial pressing method was applied to shape the SiC powder, a pressing mold was used to hold the SiC powder and an oil-pressing machine was used to shape the green body. For each sample pellet, 0.5g powder was used and pressure was controlled at 250~300Mpa. The obtained pellets were placed in a carbon crucible and then put into a vacuum furnace to pre-
sintered at 1500°C for 2 hours. Pre-sintering process was shown in Figure 2.4(a), the thermal processes including a) Ramping from room temperature to 505 °C with 15 °C per minute; b) Dwell at 505 °C for 60 minutes; c) Ramp to 1500 °C with 10 °C per minute; d) Dwell at 1500 °C for 2 hours. Then automatically cool to room temperature.

**Figure 2.4** Thermal processing of SiC pellets: a) pre-sintering b) Infiltration sintering.

*Polymer infiltration and pyrolysis:*

AHPCS was infiltrated into the pre-sintered SiC ceramics under vacuum at room temperature for 4–6 hrs, until no air bubbles were observed coming out from the pellets. For nanoparticle addition, Ni nanoparticle was dispersed in ethanol (0.1 g/ml) and infiltrated into SiC pellets and then dried at room temperature. Subsequently, AHPCS was infiltrated into the SiC pellets containing nickel. This 2-step process helps to uniformly distribute Ni nanoparticles inside porous SiC bulk (Ni-AHPC SiC). Infiltrated samples were pyrolyzed at 1200 °C or 1275 °C for 1 hour. The thermal processes were shown in Figure 2.4(b), including a) Ramping from room temperature to 650 °C with 1 °C/minute; b) Dwell at 650 °C for 15 minutes; c) Ramp
to 1200/1275 °C with 5 °C/minute; d) Dwell at 1200/1275 °C for 60 minute. Then, the thermal process ends and system automatically cool to room temperature. The polymer pyrolysis process required a very slow ramping rate (1°C/min) under 650 °C due to the thermal decomposition of polymer inside the chamber which create large amount of gaseous species, higher ramping rate will make it difficult to control the internal pressure. Such infiltration cycles were repeated 7 times.

2.2.2. Sample Characterization

The density and porosity of SiC samples were measured using the Archimedes method. Porous bulk samples were measured weight at three different conditions in order to get the necessary data for bulk density (apparent density) and porosity calculation. The three cases weight including:

a) Dry weight: clean the surface species and dry, measure dry weight. \( (m_1) \)

b) In liquid weight: sink bulk sample into water, pump for 6 hours and measure with special kit for in liquid weight. \( (m_2) \)

c) Wet weight: sample was taken out of liquid and used tissue to clean the droplets, then measure the wet bulk weight. \( (m_3) \)

Relative density=Apparent density/Theoretical density:

Which is:

\[ \phi_s = \frac{V_s}{V_t} = \frac{(m_1/\rho_t)}{(m_3-m_2)} \]  

(2-1)
Meanwhile, open porosity:

\[ \phi_p = \frac{V_p}{V_t} = \frac{(m_3 - m_1)}{(m_3 - m_2)} \] (2-2)

Close porosity:

\[ \phi_c = 1 - \phi_s - \phi_p = \frac{(m_1 - m_2 - m_1/\rho_t)}{(m_3 - m_2)} \] (2-3)

Here, \( V_s \) is solid volume, \( V_p \) is open pore volume and \( V_c \) is close pore volume. Also, \( \rho_t \) is theoretical density, and \( \rho_0 \) is water density which is 1 g/cm\(^3\) and already eliminated in equations.

In addition, the theoretical density of samples changed after multi-PIP cycles as more polymer derived amorphous SiC was formed, so the actual theoretical density slightly decreased with number of PIP cycles. The \( \rho_t \) number for each PIP cycle was calculated on the assumption that pores were fully filled with AHPCS and a yield rate of AHPCS to SiC was 75% in weight.

In this study, the theoretical density of infiltrated SiC samples were calculated. For this purpose, following assumptions were made for an ideal PIP model:

a) Pores were completely filled with polymer during infiltration steps. (In real experiments the infiltration is always not completely filled pores due to pump limitation.)

b) All Ni nanoparticles reacted with allylhydridopolycarbosilane (AHPCS) to form NiSi with the density of 7.4 g/cm\(^3\). (In real experiments, it forms both NiSi and Ni\(_2\)Si phases, but the density of two phases were similar.)

c) Open pores in SiC bulk materials were not closed during multi-PIP cycles. (In real experiments, close pores formed after some PIP cycles.)
d) The ratio of infiltrated Ni and AHPCS was constant during each PIP cycle. (Ni:AHPCS = 1:10 in weight). (In real experiments, Ni precipitation occurred during long time infiltration so it’s hard to control a constant Ni ratio for each PIP cycle.).

e) It is assumed that only non-crystalline AHPCS reacts with Ni nanoparticle during heat treatment.

The following equation describe the composition of ideal SiC bulk after PIPed, which can be considered as a combination of SiC-crystal, SiC-amorphous and NiSi, VR is the volume ratio of each component.

\[ \rho_t = \rho_{\text{crystal}} * V_R^{\text{crystal}} + \rho_{\text{amorphous}} * V_R^{\text{amorphous}} + \rho_{\text{NiSi}} * V_R^{\text{NiSi}} \] (2-4)

In this model, the amount of PDC after each step can be calculated by the ratio of open porosity. For a single PIP cycle, when open porosity is \( \phi_p \), volume of open pores is \( V^* \phi_p = V_p \).

After infiltration, remaining materials include: (a) AHPCS with volume of \( 89/90V_p \); (b) Ni with volume of \( 1/90V_p \) (10wt% of AHPCS); and (c) SiC crystal unchanged.

After pyrolysis steps, each component have the following change in volume ratio:

(a) AHPCS \( \rightarrow \) a-SiC, yielding rate 75%.

\[ V_{a\text{SiC}} = \frac{0.75}{2.9} * \frac{89}{90} V_p = 0.259V_p \] . (2-5)

(b) Ni \( \rightarrow \) NiSi.

\[ V_{\text{NiSi}} = \frac{1}{90} V_p * \frac{86}{58} * \frac{8.9}{7.4} = 0.02V_p \] . (2-6)

(c) SiC crystal unchanged.
The total increase in volume after a single PIP cycle is:

$$0.259 V_p + 0.02 V_p = 0.279 V_p.$$ \hspace{1cm} (2-7)

Here we can use $V_{pi}$ to describe the open pore volume after $i^{th}$ times PIP cycles, while $p_i$ is the open porosity.

The relative density can be written as: $\emptyset_s = \frac{V(\text{solid})}{V(\text{total})}$.

Then, the ideal relative density after $i^{th}$ PIP cycle can be written with a recursive equation:

$$\emptyset (i) = \emptyset (i - 1) + (1 - \emptyset (i - 1)) \times 0.279$$ \hspace{1cm} (2-8)

By knowing the initial porosity of SiC bulk, the theoretical density of SiC after each PIP cycle can be directly simulated with the above equations, and this number will used in Archimedes method for accurate relative density and porosity measurement.

The crystal structure of the pyrolyzed and sintered samples were examined using X-ray diffraction (XRD, D8 Bruker). It was possible to detect the presence of nickel, nickel silicide and nickel carbide phases. Scanning electron microscope (SEM, Zeiss Sigma 500 VP) was used to study the microstructure of pyrolyzes samples using sections parallel and perpendicular to the pressing direction.
2.3 Results and Discussion

2.3.1 Traditional PIP method of SiC

As reported traditional PIP method used AHPCS as preceramic polymer for densification. In this section, SiC green body shaped with uniaxial pressing was processed after a maximum of 7 PIP cycles with pure AHPCS and no aids materials. To evaluate the efficiency of experimental PIP process, an ideal infiltration model was built, and the bulk relative density of ideal model and experimental results were shown in Figure 2.5. The dash line refers to ideal infiltration model, which assume that infiltration of porous green body is 100% filled, meanwhile pores were not closed after multi PIP cycles. The solid line is the real experimental SiC pellets after 7 PIP cycles with pure AHPCS. The slope of the real density curve was comparable with ideal model in the initial 3~4 cycles, but quickly decreased to almost zero after 5 cycles. The dramatic decrease in density slope of PIP process is considered to have direct relation with blockage of open pores. In polymer infiltration model, the polymer derived ceramics formed a thin layer covering the surface of crystal SiC particles, and gradually decreased the pore size of porous matrix. However, this process will block the open pores after multi cycles repeated infiltration and pyrolysis. Once the open pores get closed, efficiency of PIP process decreased dramatically, and quickly decreased to zero after 1~2 PIP cycles, the density at this circumstance is considered as the limitation of traditional PIP process [16,18,22,29].
2.3.2 Ni Effect in PIP Process of SiC Densification.

In order to study the effect of Ni nanoparticle additions on the bulk density and microstructure, SiC green body pellets were pre-sintered and then infiltrated with Ni nanoparticles and AHPCS polymer, as explained in the experimental section (2.2). Figure 2.6 shows the bulk density and open porosity of SiC ceramics after the pyrolysis and sintering at 1200 °C or 1275 °C. Two pyrolysis temperatures were chosen, because the melting temperatures of expected nickel silicide phases were 990 °C (NiSi) and 1255 °C (Ni₂Si). The density of SiC samples was measured after each PIP cycle was finished. The density of pre-sintered SiC preform was 1.836 g/cm² which was 57.2% of the theoretical density of SiC. After 7 PIP cycles using the pure-AHPCS and the sintering temperature of 1200°C, the open porosity of samples...
was 13.75%. The bulk density was 2.769 g/cm² which was 85.4% of the theoretical density of crystalline SiC (particles) - amorphous SiC (precursor) composites on the assumption that all pores between the SiC particles were completely filled with amorphous SiC. An increase in the pyrolysis temperature to 1275 °C caused a negligible change in the relative density of samples using pure AHPCS (from 85.4% to 85.5%). In the case of pure AHPCS, the efficiency with which a new PIP cycle resulted in an increase in the bulk density decreased considerably after the first 4 PIP cycles (Figure 2.6(b)). If the open pores are not closed during the PIP, one would expect that the efficiency in Figure 2.6(b) is maintained at 34%, regardless of the number of the PIP cycles. Hence, a decrease in the infiltration efficiency suggest that repeated PIP cycles start to close pores near the surface and block the penetration of the polymers from the surface to the inner part of the bulk.
Figure 2.6 (a) Overall porosity (solid line) and bulk density (dash line) of pyrolyzed samples (infiltrated with pure AHPCS or Ni-AHPCS mixture) vs PIP cycles, (b) a decrease in the fraction of open porosity removed in an infiltration cycle with increasing number of PIP cycles.
The microstructure of pyrolyzed SiC samples using pure AHPCS is shown in Figure 2.7. This was obtained from a cross-section which is parallel to the pressing direction. When pure AHPCS was infiltrated and pyrolyzed 7 times, the near-surface and inner regions exhibit different microstructures. The microstructure of the near-surface region is dense, but large pores are easily observed in the inner bulk region. This supports that AHPCS fills interparticle pores in the near-surface region well, but the penetration of polymers into the center of samples was prevented. This leaves pores in the center region partially filled.

![Figure 2.7](image)

Figure 2.7 Microstructure of pyrolyzed SiC sample at 1200 °C: a) low magnification image of the section, b) higher magnification of a dense region, c) higher magnification of a porous region.

In contrast, the infiltration of Ni nanoparticles and AHPCS clearly increases the density of samples by improving the infiltration efficiency particularly during later PIP cycles. After the sequential infiltration of Ni nanoparticles and AHPCS and the following pyrolysis were repeated
7 times, the porosity decreases to 11.86% (1200 °C pyrolysis) and 7.65% (1275 °C pyrolysis). It is noted that the density of SiC ceramics was above 90% after 7 PIP cycles with pyrolysis and sintering at 1275°C. This has not been achieved in most previous PIP studies where the density ranges from 75% to 85% [20~22]. Figure 2.8(a) and (b) show the microstructure for samples infiltrated with nickel and AHCPS and sintered at 1200 °C while Figure 2.8(c) and (d) show the microstructure of samples infiltrated with Ni nanoparticles and AHCPS and sintered at 1275 °C. The addition of Ni nanoparticles results in more uniform and dense microstructures near the surface and in the interior. The overall microstructure became denser and no large unfilled pores were presented. Sections between the crystalline SiC grains were observed with better filling status and smaller pores. This suggests that the addition of Ni nanoparticles suppresses the blockage of pores during repeated infiltration cycles and the preceramic polymer is uniformly distributed in the interior part of samples.

Interestingly, the density of Ni and AHPCS infiltrated samples is dependent on the sintering temperature, which is not observed in samples infiltrated with only AHPCS. To understand the difference in the effect of the sintering temperature, the phase distribution in sintered samples was examined using XRD.
Figure 2.8 Microstructure of SiC samples infiltrated with Ni nanoparticles and AHPCS:

a)~b) at 1200 °C; c)~d) at 1275 °C.

Figure 2.9 shows XRD pattern of SiC samples infiltrated for 7 PIP cycles with pure AHPCS or Ni particles and AHPCS and subsequently sintered at 1200 or 1275 °C. The XRD patterns of pure-AHPCS infiltrated SiC exhibits only crystalline SiC, regardless of the pyrolysis and sintering temperature. In contrast, when Ni-AHPCS was infiltrated, there is a dependence of the crystal structure on the pyrolysis and sintering temperature. In samples of 1200 °C, XRD peaks of Ni$_2$Si and NiSi phase were observed, suggesting that at 1200 °C, the reaction is sluggish and the initially formed Ni2Si is still present after few hours heat treatment. Hence, not all the nickel addition is presented as a liquid phase. As the temperature increased to 1275°C, the XRD peaks of Ni$_2$Si
Almost disappeared and only NiSi peaks were found, this suggests that Ni2Si continues to react with amorphous SiC phase that derived from polymer in PIP cycles to form NiSi. Given that Ni2Si and NiSi have different melting temperature (1255 °C and 990 °C), XRD analysis results of Ni nanoparticle added samples suggest: (i) a liquid phase appeared during sintering, 2) a reaction of NiSi melt with Ni nanoparticles or amorphous SiC form Ni2Si phase formed on heating NiSi, and 3) the amount of the liquid phase increased at 1275 °C which is higher than the melting temperature of Ni2Si and NiSi. This liquid phase of nickel silicide then wets the silicon carbide grain and is uniformly distributed throughout the material under surface tension. The liquid then redistributes the fine amorphous SiC particles created by the PIP and thereby mitigating the blockage of pores between the larger silicon carbide grains used in the preparation of the green compact. This promotes the redistribution of infiltrated materials toward inner pores, leading to the increase in the density of the final SiC ceramics.

Based on XRD patterns and the reported melting temperature of nickel silicide phases, chemical reaction pathways of infiltrated materials can be written as follows:

\[
\text{AHPCS} \rightarrow \text{amorphous SiC (gradual transition)} \quad (300 \sim 900 \, ^{\circ}\text{C}) \quad (2-9)
\]

\[
\text{Ni} + \text{Si(in AHPCS)} \rightarrow \text{Ni}_2\text{Si(s)} \quad (>820 \, ^{\circ}\text{C}) \quad (2-10)
\]

\[
\text{Ni} + \text{Si(in AHPCS)} \rightarrow \text{NiSi(s)} \quad (<940 \, ^{\circ}\text{C}) \quad (2-11)
\]

\[
\text{NiSi(s)} \rightarrow \text{NiSi(l)} \quad (>990 \, ^{\circ}\text{C}) \quad (2-12)
\]

\[
\text{Ni}_2\text{Si(s)} \rightarrow \text{Ni}_2\text{Si(l)} \quad (>1255 \, ^{\circ}\text{C}) \quad (2-13)
\]

\[
\text{Ni}_2\text{Si(l)} + \text{Si (in amorphous SiC)} \rightarrow \text{NiSi(l)} \quad (1255\sim1275 \, ^{\circ}\text{C}) \quad (2-14)
\]

Given that Ni2Si and NiSi have different melting temperature (1255 °C and 990 °C), XRD analysis results of Ni nanoparticle added samples suggest: 1) a liquid phase appeared
during sintering, 2) a reaction of NiSi melt with Ni nanoparticles form Ni$_2$Si phase formed on heating NiSi, and 3) the amount of the liquid phase increased at 1275 °C which is higher than the melting temperature of Ni$_2$Si. This liquid phase of nickel silicide mitigates the blockage of pores and promotes the redistribution of infiltrated materials toward inner pores, leading to the increase in the density of final SiC ceramics.

**Figure 2.9** XRD pattern of SiC samples (after 7 PIP cycles) infiltrated with pure AHPCS or Ni particle - AHPCS mixture and then pyrolyzed at 1200 or 1275 °C. a) long scan range; b) short scan range.

A positive effect of nickel silicides on open pore filling is schematically explained in Figure 2.10. The preceramic polymer that fills the pores between SiC particles shrinks by 70 vol%, and transforms to amorphous SiC during the pyrolysis. If this conversion of AHPCS to amorphous SiC occurs uniformly, pore channels between SiC particles should stay open. However, relatively narrow pore channels are often blocked (Figure 2.7(a)), as reported in
previous studies [21,22]. Once the pores closer to the sample surface become closed, the polymer is not able to infiltrate into the interior of the bulk material. In contrast, if the nickel silicide phase of low melting temperature is formed by the infiltration of AHPCS and Ni nanoparticles, the silicide melts during the pyrolysis step. The liquid phase is formed and is thought to help the redistribution of infiltrated materials under the surface tension of liquid phase. Hence, fine pore channels are not fully blocked, as illustrated in Figure 2.7(b). This explains an increase in the density of samples by the sequential infiltration.

**Figure 2.10** Schematic diagram of SiC infiltration mechanism.
2.4. Conclusion

In this chapter, porous SiC ceramics were infiltrated using pure polymer precursor AHPCS or precursor containing additional Ni. The PIP process was repeated up to 7 cycles and the effect of additional Ni nanoparticle as sintering aids was presented. Ni nanoparticles caused the formation of nickel silicide phases that could provide a liquid phase on the pyrolysis over 1200 °C due to the formation and melting behavior of NiSi and Ni$_2$Si phases. These silicide phases provide unblockage of open pores that would have been blocked at no Ni case, and substantially increased the relative density of the final SiC ceramic to be higher than 90% after 7 PIP cycles. The increase of pyrolysis temperature from 1200 °C to 1275 °C also showed a positive impact on the amount of melted silicide phases which presented a clear improvement in the density growth rate of Ni added SiC samples.
Chapter 3 Effect of carbon additives in PIP process of nanoparticle added SiC densification

3.1 Introduction

3.1.1 Additional Carbon Nanoparticle in PIP Process

In this chapter, the effect of additional carbon on the phase transition of the preceramic – Ni mixture during the pyrolysis is investigated to analyze the reaction pathways and provide SiC ceramics of high density and outstanding mechanical properties. While the low melting point liquid phase is advantages for improving the density of the PIP SiC, the presence of those components would be detrimental to high temperature properties. To address this issue, carbon nanoparticles, selected to react with nickel silicide phases and thereby decrease the amount of liquid after several PIP cycles.

The underlying hypothesis is that nickel silicide in SiC matrix can react with carbon nanoparticles and return to SiC and other carbide phases. If then, sequential infiltration of the preceramic – Ni nanoparticle mixture and the preceramic – carbon mixture during the PIP process enables the manufacturing of dense SiC ceramics with higher purity and good high-temperature strength.

3.1.2 Reaction Pathways in Ni-C System

Pure carbon particles cannot easily react with Ni particles around the temperature of given pyrolysis process parameters. Figure 3.1 shows the phase diagram of Ni-C system which suggests that no stable Ni$_3$C phase was observed in low carbon range. However, the melted nickel silicide liquid phase has much higher active energy to provide reaction pathway with carbon nanoparticles and thus reduced nickel silicide back to silicon carbide and nickel carbide
phases. In previous reports, the nickel carbide (also known as Ni(C) solid solution) can be produced by reaction between Ni nanoparticle or Ni thin film and CO gas at relative low temperature (~450 °C), it was considered as a metastable phase and can decompose during high temperature (>550 °C) [76]. Another method of Ni₃C formation used Ni(111) crystal as substrate and reacted with carbon source [77]. In this method, thin film Ni was thermally evaporated under high temperature annealing onto substrate such as rock salt, then deposited to form single crystal Ni film. This greatly improves the contact surface between Ni and carbon sources during the reaction under a low ramping rate annealing (300~500 °C). The carbon source can be either CO gas with low flow rate or thin carbon film under vacuum environment (~10⁻⁴ Pa) [76,77]. The lattice structure of Ni₃C was shown in Figure 3.1(a). Nickel has to rearrange from a cubic close lattice into a trigonal structure with a hexagonal close packing of Ni and C in octahedral sites.

Figure 3.1 (a) Lattice structure of the metal (dark gray circles) and carbon (light gray circles) occupies octahedral sites in Ni₃C; (b) Phase diagram of Ni-C system. [78]
Preparation and synthesis of different format Ni$_3$C nanomaterials have been reported, including nanoparticles, nanowiskers, nanowires, core-shell nanochains and nanocrystals. Several strategies for the synthesis of Ni$_3$C including mechanical alloying [77], spray pyrolysis [87], carbon-ion implantation [86], and chemical synthesis [88]. In previous studies, Leng et al. fabricated Ni$_3$C NPs by thermal decomposition of nickel formate in organic solution in the presence of oleic acid and oleylamine, demonstrating the Ni$_3$C formation by a catalytic and diffusion reaction mechanism [88]. Wiltner et al. deposited carbon films on Ni crystal substrate and thermal annealed up to 970K for carbide formation [77]. The carbide layer is located between deposited carbon layer and metal substrate, then characterized with XRD and XPS to confirm the existence and purity of Ni$_3$C. Kim et al. developed an advanced two-step chemical solution method of core-shell Ni$_3$C/C nanoparticles under a comparatively low temperature of 523K. Prepared Ni NPs were transferred to a triethylene glycol (TEG, C$_6$H$_{14}$O$_4$) solution that contained a small amount of NaOH. NiCs were obtained by heating the solution to 523K at a heating rate of 8K/min, and a simple diagram of Ni$_3$C NPs growth mechanism was shown in Figure 3.2 [89].

In this chapter, carbon nanoparticles were added into Ni-PIPed SiC bulk samples through the infiltration process and evenly filled the pores after the 4th PIP cycle. The later 3 cycles will be C-PIPed and aiming for the reaction between nickel silicide phases and carbon NPs to form Ni$_3$C phase and reduce nickel silicide phases. After 7 PIP cycles finished, XRD and SEM characterization of final SiC bulk samples were collected and compared with traditional PIP method. Results of SiC samples characterization provide evidence to show the existence of stable Ni$_3$C phase in the SiC matrix after multi-PIP cycles, also help the analysis on reaction pathways of Ni-Si-C system during thermal processing.
3.2. Experiment

The PIP process of carbon nanoparticle added PIP process was same as Ni nanoparticle added PIP case for the former 4 cycles. Two-step infiltration was applied which Ni nanoparticle was dispersed in ethanol (0.1 g/ml) and infiltrated into SiC pellets and then dried at room temperature. Subsequently, AHPCS was infiltrated into the SiC pellets containing nickel.

After SiC samples were infiltrated with Ni added AHPCS for 4 PIP cycles, carbon nanoparticles (2.5wt% of AHPCS) were added into SiC samples from 5th PIP cycles to replace Ni, with the same two-step infiltration method as Ni nanoparticles. To explore the effect of carbon nanoparticles on the formation of different silicide or carbide phases, the pyrolysis was performed at both 1200 °C and 1275 °C.

The crystal structure of the pyrolyzed and sintered samples were examined using X-ray diffraction (XRD, D8 Bruker). Scanning electron microscope (SEM, Zeiss) was used to study the
microstructure of pyrolyzes samples using sections parallel and perpendicular to the pressing direction.

3.3 Result and Discussion

Figure 3.3 shows the porosity and relative density of the samples which were infiltrated with Ni-AHPCS for the first 4 cycles and C-AHPCS for the last 3 cycles. The pyrolysis and sintering steps were performed at both 1200 °C and 1275 °C. Compared with fully Ni-added PIPed SiC samples, the replacement of Ni nanoparticles to carbon in the 5th – 7th PIP cycles cause only a small change in the porosity and density. As the density was slightly decreased and porosity increased, this can be considered with the lack of Ni source and the decrease of transient liquid phases in high temperature annealing. While amount of liquid phases decreased, open pores and pore channels start to block and more close pores formed. As a result, the density slope become much smaller than fully Ni-added samples, more similar to pure AHPCS case SiC density slope. In Figure 3.2(b), change of rate of porosity dropped rapidly after 4th PIP cycles and finally reached almost zero after 7 cycles. This result present the density limitation of these SiC samples with the given PIP method. Even provide with more PIP cycles, the density won’t have much improvement.

Also, the effect of sintering temperature on the density was clearly observed. The difference of 1200 °C and 1275 °C on Ni-C-added PIPed samples showed similar results as fully Ni-added samples. The higher temperature is just above the melting point of Ni$_2$Si, while the lower temperature is just below the melting point. This results in different amount of liquid phase during annealing, and thus show different density slope along the PIP cycles.
Figure 3.3 (a) Density vs PIP cycles of SiC pellets with additional Ni and carbon in polymer infiltration. (b) a change in the rate of porosity elimination with increasing number of a PIP cycle.
Figure 3.4 shows XRD patterns of samples which were infiltrated with Ni nanoparticle-AHPCS for the 1\textsuperscript{st} – 4\textsuperscript{th} PIP cycles and carbon nanoparticle-AHPCS for the 5\textsuperscript{th} – 7\textsuperscript{th} PIP cycles. While the replacement of Ni nanoparticles by carbon nanoparticles in the 5\textsuperscript{th} – 7\textsuperscript{th} PIP cycles does not change the density, it causes a considerable change in the composition and content of 2\textsuperscript{nd} phases. When carbon nanoparticles were added and pyrolyzed, Ni$_3$C peaks appeared and the intensity of Ni$_2$Si and NiSi peaks decreased.

Figure 3.4 XRD pattern of SiC pellets with Ni and C addition after different PIP cycles (1275 °C). a) long scan range; b) short scan range.

The cross-section SEM image of thermally etched Ni-C-AHPCS samples which were sintered at 1200 °C and 1275 °C are presented in Figure 3.5. Compared with the microstructure of Ni-AHPCS samples in Figure 2.3, the addition of carbon nanoparticles results in slightly more porous amorphous SiC, containing fine particles between the crystalline SiC particles. The fine
particles could be Ni$_3$C phase that precipitated within the amorphous SiC during cooling due to the presence of nickel silicide and excess carbon.

![Image](image.png)

**Figure 3.5** Microstructure of SiC sample treated with Ni-AHPCS for the 1$^{st}$-4$^{th}$ PIP cycles and with C-AHPCS for the 5$^{th}$-7$^{th}$ after pyrolyzed at a, b) 1200 °C and c, d) 1275 °C.

When carbon nanoparticles were used in the PIP process, Ni$_3$C is formed during the pyrolysis through the reaction of NiSi (or Ni$_2$Si) and carbon. Melted NiSi and Ni$_2$Si phases mixed with carbon nanoparticles during the thermal process and react to give nickel carbide. During the replacement reaction, Si was replaced by carbon and mixed with unreacted liquid
phase, the liquid then fluid inside matrix due to the pressure gradient and collect extra carbon, and helps the Si react with carbon to become SiC. This reduces the amount of silicide phases which melts at relatively low temperature. Given that low melting temperature phases reduce mechanical strength at high temperature due to a creep behavior [25], carbon addition may help to improve the mechanical properties of SiC ceramics manufactured with the PIP method. The proposed reaction mechanism using the formation of the Ni$_3$C phase was also confirmed by reacting of AHPCS (amorphous SiC), Ni nanoparticles and C nanoparticles.

With additional carbon nanoparticles additive from 5 to 7th PIP cycles, carbon nanoparticles mixed with liquid silicide phase and became transient liquid mixture NiSi(C). During high temperature pyrolysis process, liquid nickel silicide reacted with carbon nanoparticle and formed Ni$_3$C phase, considered as following reactions:

\[
\text{NiSi(l)} + \text{C(s)} \rightarrow \text{SiC} + \text{Ni}_3\text{C} \quad (3-1)
\]

\[
\text{Ni}_2\text{Si(s)} + \text{C(s)} \rightarrow \text{SiC} + \text{Ni}_3\text{C} \quad (3-2)
\]

An additional supplemental process was applied on SiC amorphous powders to further prove the reaction pathway of Ni$_3$C formation. The XRD of each group sample was shown in Figure 3.6. The black curve in Figure 3.6 is thermal annealed AHPCS, also called polymer derived ceramics (PDCs), which is mainly low crystallinity SiC and amorphous SiC. While PDC-SiC was mixed with SiC crystal or SiC bulk materials, these broad peaks couldn’t be distinguished as they overlapped with 6H-SiC crystal phase peaks. This is the reason that Figure 2.9 and Figure 3.3 didn’t have the result of these broad peaks. In this supplemental process, no SiC crystal particles were used, thus no SiC crystal peaks will be detected in XRD results.
After mixing this PDC powder with Ni nanoparticles and applied with thermal process at 1200 °C, new crystal phases appeared as NiSi and Ni$_2$Si shown in red curve, which is consist with former results in chapter 2. Then, additional carbon nanoparticles were mixed with NiSi/Ni$_2$Si-PDC powder and further applied with a thermal process. The XRD pattern showed clearly on blue curve that Ni$_3$C phase formed even in a powder mixed sample. Which provide solid evidence to prove the formation and stability of Ni$_3$C with reaction equations (eq 3-1,3-2).

**Figure 3.6** XRD pattern of AHPCS-derived-SiC mixed with additional Ni and carbon nanoparticles after multi-cycle heat treatment (1200 °C).
3.4 Conclusion

In this chapter, additional carbon nanoparticle was applied on previous Ni-PIP ed SiC material. The density and microstructure of the Ni added SiC and Ni-C added SiC after multi-PIP cycles were compared and analyzed. Replacement of Ni nanoparticles by carbon nanoparticles in the 5–7th PIP cycles did not show significant change on the density of final SiC ceramics, but otherwise reduced the amount of the nickel silicide ceramics, due to the formation of Ni$_3$C phase. XRD results provide clear evidence on the formation and thermal stability of Ni$_3$C phase after the thermal processes in both SiC green body matrix and SiC powder samples. Different from low temperature gaseous reaction of Ni$_3$C prepared from Ni nanoparticle and CO in 400–500 °C [76], the solid-liquid state reaction between NiSi and excess carbon nanoparticles in this chapter provide higher thermal stability of Ni$_3$C as a reduction product between transient liquid phases (NiSi and Ni$_2$Si) and carbon in PIP process. The sequential infiltration of PIP SiC with nickel and carbon nanoparticles resolve the disadvantage of Ni-PIP method that will create certain amount of low melting transient phases remaining in final SiC products that show negative mechanical behavior in high temperature applications.
Chapter 4 Advanced Densification Technique on SiC Binder-Jet Printing Matrix via Polymer Infiltration and Pyrolysis

4.1 Introduction

4.1.1 BJ3DP of SiC Ceramics.

In ceramic processing from powder feedstock, powder pressing has the advantage of fast speed, low cost and mass production, but there is a limitation in the shape that the powder pressing can produce. Additive manufacturing methods allow for preparing the green body of more complex shapes from ceramic powders, and reduce the constraints in the shape design of the ceramic materials [28]. Among all developed additive manufacturing techniques, binder-jet 3D printing (BJ3DP) has the most complete developed device for production, together with advantages of controllable printing parameters and avoid the need of supporting materials. In addition, BJ3DP can be applied to large shapes and possess the fastest printing speed among all AM technique [29,30].

However, BJ3DP is limited by the high volume of pores and consequent low density due to the limited packing factor of powder materials [31]. Moreover, high volume shrinkage is observed during post-processing resulting in dimensional inaccuracy and creep formation [32]. The presence of porosity makes the printed parts brittle and has a negative effect on mechanical properties. Silicon carbide ceramics have been studied for decades because of their excellent mechanical strength and high thermal conductivity. For the densification of SiC ceramics, several techniques such as high temperature sintering, reaction sintering and polymer infiltration pyrolysis have been studied [13,15].
4.1.2 PIP Process of BJP-SiC with Sintering Aids.

The high temperature sintering technique is not suitable for binder-jet printed green bodies of large SiC particles, since their relative density is near 50% [13,15]. Even the combination of high sintering temperature (above 1800 °C) and sintering aids (such as Al₂O₃ and BC) are not good enough to fully densify loosely packed SiC green bodies. While these dopants may assist solid-state sintering by the creation of vacancies, aluminum and boron are also known to result in liquid phases that accelerate sintering and also accelerate the phase transformation in SiC [26,33]. Such a difficulty in the sintering of binder-jetted green bodies of large SiC particles can be mitigated by using reaction sintering or infiltration or polymer infiltration. In the reaction sintering process, a mixture of SiC and carbon (C) particles is shaped first. This preform is infiltrated with liquid silicon (Si). Carbon in the preforms reacts with liquid Si to form SiC which bonds the pre-existing SiC grain and eventually fill pores with SiC. The temperature required for the reaction sintering of SiC is above the melting temperature of Si (i.e. 1410 °C) [34]. Finally, SiC ceramics can be made by infiltration of SiC compacts with polymer precursors (e.g. polycarbosilanes (PCS) or allylhydridopolycarbosilane (AHPCS)) that form silicon carbide much below 1410 °C [17,18,19,35]. While polymer infiltration and pyrolysis (PIP) method considerably decreases the densification temperature, PIPed SiC ceramics is lower than 90% [18~22]. The conversion of preceramic polymers to SiC shrinks polymers inside the ceramic matrix and leaves pores.

This low-density issue of PIPed SiC ceramics gets more serious when BJ3DP is used to prepare SiC green bodies, as schematically explained in Figure 4.1. In binder-jetted green bodies of large SiC particles, the loosely packed region is found between each printing layer. This loosely packed region results in the microcracks in final PIPed SiC ceramics. In our recent study,
more polymer precursor tends to accumulate in the interlayer region, fill it up with amorphous SiC, and lower the permeability for gas release. Accumulated gas pressure in the interlayer region eventually creates cracks, forms extended pore channels, and increases the non-uniformity of the microstructure of SiC ceramics. This locally damaged microstructure was detected on reconstructed CT cross sections.

![Diagram](image)

**Figure 4.1** A schematic showing printing defects between two spread layers and the effect of PIP and resulting gas cracks [38].

In order to increase the bulk density of binder-jetted SiC ceramics by PIP process, nickel (Ni) and carbon (C) nanoparticles can be mixed with AHPCS. Ni nanoparticles help the formation of a transient liquid phase by reacting with AHPCS in the pyrolysis step. This liquid phase prevents the interlayer pores from being fully filled with amorphous Si and leaves pore channels open for the release of burn-out gas. This can improve the final density and mechanical properties of PIPed SiC ceramics [24,63].
4.1.3 SPS Technique of SiC

A potential disadvantage of PIP process on low density green body samples is the long processing time. In this study, one PIP cycle took 22~24 hours from starting infiltration to the end of pyrolysis. While this cycle repeated for more times, the entire process of a single sample took more than 1 week processing, which limits the efficiency of lab manufacturing. To improve the efficiency of high density SiC bulk sintering, an advanced technique known as spark plasma sintering (SPS) was introduced into sintering process. SPS is a sophisticated consolidation technique which typically utilizes pulsed DC current-induced joule heating coupled with high pressures [79]. Additionally, a T-shape punch can be used on the sample die for a pressureless spark plasma sintering (PSPS). Up to date, the highest density achieved by sintering SiC with liquid phase, oxide aids have reached 94% for SPS technique, and 88% for PSPS technique, the holding temperature was around 1400~1600 °C [80~83]. The design of different dies and molds are shown in Figure 4.2. Regular SPS using straight graphite punch on both top and bottom of sample powder then applied pressure from 10~1000 Mpa range during heating. This would help form close packing of bulk materials which similar as an uniaxial pressing or hot pressing sample. While electric current goes through the powder, high power heating energy was applied and help sintering the samples. For PSPS case, T-shape punch was used on top and bottom of powder sample, and the pressure was limited under 0.75Mpa which is more suitable for shaped bulk samples. For fully fill of inside area, same type of unshaped powder and sintering aids (like B, C and metal oxides) were used to cover the bulk samples and sintering with electric field assist heating process [79, 80].

The importance of the SPS method as a tool of consolidation of powder process has been demonstrated by the large number of studies in past decades [90]. Compared with traditional
methods such as hot pressing or pressureless sintering, the advantages of SPS process including cleaner grain boundary in ceramic materials [91,92], a remarkable increase in super-plasticity of ceramics [93], higher permittivity in ferroelectrics [94], improved magnetic properties [95,96], improved bounding quality [97], improved thermoelectric properties [98] and reduced impurity segregation at grain boundaries [98,99]. The characterization of SPS process have been reviewed by researchers [90]. The most important aspects of SPS include (1) a high heating rate; (2) the application of pressure; (3) the effect of current.

**Figure 4.2** Die designs of regular and pressureless SPS: a) pressureless form of SPS using T-shaped punches, b) regular SPS subjected to applied external pressure, and c) another form of pressureless SPS with an additional graphite piece [84].

*The effect of heating rate.* Heating rate is one of the most significant difference between SPS sintering and hot-pressuring method. In the former heating rate can achieved as high as 1000 C/min. The effect of heating rate has been investigated considerably in both pressureless and
pressure-assisted sintering. In pressureless sintering, higher heating rates have been proved to
enhance densification by by-passing the non-densifying mechanism of surface diffusion and by
creating an additional driving force due to large thermal gradients [100]. However, investigations
on the effect of heating rate on densification and grain growth in the SPS have produced
conflicting results. In the study of several ceramic materials such as alumina, zirconia and
MoSi$_2$, the density and grain growth had little or no effect at heating rate (between 50 to
300 °C/min.), and some negative effect was observed at higher heating rate (>600 °C/min) [101].
This was explained on the basis of large thermal gradients existing with high heating rates. These
in turn cause the outside of the sample to sinter while the inside still has considerable porosity
[102].

*Effect of applied pressure.* It can be easily noted that when powders are sintered under an
applied pressure, higher densification is achieved at the same temperature. For more detailed
investigation, the pressure has a mechanical role as well as an intrinsic role. Mechanically the
pressure has a direct effect on particle re-arrangement and the destruction of agglomerates,
particularly in the case of nanometric powders. The intrinsic effect of the pressure can be
assessed from the driving force for sintering:

$$\frac{d\rho}{(1-\rho)dt} = B(g \frac{\gamma}{x} + P)$$  \hspace{1cm} (4-1)

where $\rho$ is the fractional density, $B$ is a term that includes diffusion coefficient and
temperature, $g$ is a geometric constant, $\gamma$ is the surface energy, $x$ is parameter that represent a size
scale (which is related to particle size), $t$ is time, and $P$ is the applied external pressure. The left
side of this equation represents the intrinsic contribution of driving force for sintering, while
right side of equation represents the intrinsic contribution to the driving force by the applied pressure. The effect of applied pressure on sintering thus depends on the relative magnitudes of the two terms.

**Figure 4.3** (a) Effect of pressure on the temperature needed to get 95% relative density for cubic ZrO$_2$. The corresponding decrease in grain size is also shown. (b) The effect of applied pressure on the density and grain size of cubic ZrO$_2$. Constant temperature of 1200 °C, hold time 5 min, heating rate 200 °C/min.
It can also be summarized that an increased driving force for sintering as a result of the application of a pressure. This leads to a decrease in the sintering temperature and a limitation of grain growth [103], as shown in Figure 4.3(a). The effect of pressure on density and grain size when sintering was carried out at constant temperature is shown in Figure 4.3(b) for another powder of cubic zirconia [107]. It was shown that while the pressure has no effect on the grain size (dash line), it has a marked influence on the density after sintering for 5 min at 1200 °C.

**Role of the current.** In general, the use of current in thermal heating focused on the thermal effect of current. Joule heating provides high heating rates which can provide a benefit by by-passing the grain coarsening low temperature mechanisms (e.g. surface diffusion) [100]. On the other hand, further studies showed that the imposition of a current has a pronounced effect on mass transport. At the present level of understanding, the observed current’s influence on mass transport can be attributed to one of the several intrinsic effects including electron wind modification of the diffusion flux (i.e., electromigration) [104], an increase in point defect concentration [105], or a reduction in the mobility activation energy for defects [106].

In this chapter, large α-SiC particles were binder jetted to shape a green body. PIP cycles of SiC green bodies were repeated up to 7 cycles using a mixture of SiC preceramic precursor and Ni nanoparticles. In comparison to traditional PIP, a new PIP process increases the overall density of final SiC products and suppresses the appearance of large cracks. For a more efficient sintering processing, SPS step was added between 4th and 5th PIP cycle for an extremely fast sintering step that shows a competitive bulk density as a traditional 7th PIPed SiC product. Micro-CT, SEM and XRD analyses were conducted to characterize the microstructure, pore distribution, and phase evolution of SiC ceramics which were produced by traditional PIP or a new PIP process. Analysis results show that a metal silicide phase which is formed through the
reaction between the ceramic precursor and the Ni nanoparticles, melts during the pyrolysis and opens a channel for gas escape. This leads to the dense ceramic, and increases the uniformity of the microstructure.

4.2. Experiment

4.2.1 BJP Sample Preparation

Green body shaping and pre-sintering: α-SiC (400-mesh (38 μm), Sigma-Aldrich, USA) powder was used as the feedstock for binder jet printing. The printing process was carried out using the binder-jet printer (X-1 Lab printer, ExOne, USA) with the following printing parameters: 100 μm layer thickness, a computed binder saturation of 80%, a drying powder control setting of 70%, and the spread speed of 32 mm/s. Two CAD models were designed for printing. One has a cubic shape with 1×1×1 cm³, and the other has a plate shape with 1 cm in diameter and 0.3 cm in height. As-received SiC powder was fed into the binder jet printer and after printing, the build box was baked in an oven at 200 °C for 8 h for binder curing. The green body was placed in a carbon crucible and pre-sintered at 1500 °C for initial particle necking. Uniaxially pressed samples (2 tom/cm²) were also prepared as control samples.

Polymer infiltration and pyrolysis: AHPCS was infiltrated into the presintered SiC ceramics under vacuum at room temperature for 4~6 hrs, until no air bubbles were observed coming out from the pellets. For nanoparticle addition, Ni nanoparticle was dispersed in ethanol (0.1 g/ml) and infiltrated into SiC pellets and then dried at room temperature. Subsequently, AHPCS was infiltrated into the SiC matrix containing nickel. This 2-step process helps to uniformly distribute Ni nanoparticles inside porous SiC bulk (Ni-AHPCS SiC). Infiltrated
samples were pyrolyzed at 1200 °C or 1275 °C for 1 hour. Such infiltration cycles were repeated up to 7 times. Ni-AHPCS SiC samples, were then infiltrated with carbon nanoparticles rather than Ni nanoparticles in cycles 5 to 7 in order to examine the reaction of carbon with the expected nickel and silicide phases.

4.2.2 Sample Characterization

Density and porosity of samples after each PIP cycle were measured by Archimedes’ method. In addition, a theoretical density of samples was calculated for each PIP cycle on the assumption that pores were fully filled with well-mixed Ni-AHPCS and a yield rate of AHPCS to SiC was 75 % in weight. The theoretical density of infiltrated SiC materials changes between PIP cycles, since the pyrolyzed SiC solid is amorphous. Therefore, the PIPed SiC is in fact a composite of α-SiC, with a theoretical density of ~ 3.2 g/cm3, and infiltrated amorphous SiC with a theoretical density of ~2.9 g/cm3, also a small amount of NiSi solid phase with density of ~7.4g/cm3. A theoretical density along with PIP cycle is built by an excluded volume model. The derived relative density relationship between \((i-1)\)th and \(i\)th PIPed SiC samples in this study can be described as:

\[
\phi (i) = \phi(i-1) + (1 - \phi(i-1)) \times 0.279
\]  

(4-2)

Where \(\phi\) is the relative density of the sample. An illustration of this excluded volume model is shown in Fig. 4.4.
Figure 4.4 The exclude volume model of polymer infiltration and pyrolysis.

Microstructure of the as-received powder, green bodies, and PIPed samples was characterized using a SEM-ZEISS Sigma500 VP (Thermo Fisher Scientific, USA) as well as the Bruker SkyScan 1272 μCT (Bruker, USA). The crystal phase of the pyrolyzed and sintered samples were examined using X-ray diffraction (XRD, D8 Bruker). It was possible to detect the presence of nickel, nickel silicide and nickel carbide phases.

Micro-CT scan (Bruker SkyScan 1272) was performed for PIPed samples. Each sample was cut into small rod with 1mm diameter and 5mm height, and placed in a sample holder for a 360-degree scanning. From full scanning, cross-section images along the scanning directions were exported. Micro-CT analysis system was used to build a 2D slide-by-slide image set or a 3D structure for more detailed analysis. The parameters used in the CT scans are as follows: voltage and current of the x-ray source being 90 kV and 100 μA respectively, voxel edge length was 1 μm and the scanned image resolution was 2680 x 2680 pixels. After scanning, the 2D image in the XY plane was reconstructed using NRecon software, reconstructed images were then processed and analyzed using CTAn. Figure 4.5 shows the general processing of the scanned images in this work.
For 2D analysis, the solid area fraction (SAF) can be calculated for each reconstructed image by setting a threshold number of whiteness/darkness, in order to separate pores and solid area of each image. This data can be plotted against the relative height along Z-axis, forming a Z-direction SAF plot. By comparing SAF curve of SiC samples under different PIP process, the effect of PIP parameters and effect of additional sintering aids can be observed. The benefit of newly accomplished PIP method shows enhanced densification behavior on BJP samples, as well as the decrease in printed defects between layers.

Figure 4.5 The μCT workflow applied in this work.
4.3 Results and discussion

4.3.1. PIP Method on BJP-SiC Samples with Sintering Aids.

Figure 4.6 shows the relative density and porosity of PIPed samples which were prepared using BJP and pressing, as a function of PIP cycles. After 1500 °C pre-sintering, BJP SiC and pressed SiC have a relative density of 48% and 56%, respectively. At this porosity level, all pores are considered as open pores. From the 1st to 4th cycle, the relative density of pressed samples increased by ~7% per each PIP cycle. This constant densification rate suggested that pores were not closed and remained open until PIP cycles were repeated 4 times. From the 4th to 7th PIP cycle, the increase rate of the density per cycle decreased from 16.1% to 5.7% for pressed sample and 16.0% to 4.2% for BJP sample (Fig. 4.8(b)), which implies that a part of pores is clogged during PIP process and the closed pores appeared. From the 4th to 7th PIP cycle, the apparent density which was calculated by sum of relative bulk density and open porosity, decreased from 99.7% to 96.9%. A volume difference of 3% as attributed to the volume of close pores. In comparison to pressed SiC samples, the density of BJP3D SiC samples is smaller. This is because the packing of large SiC particles is poor in BJP process. It is noted that saturation of the density as a function of PIP cycle was not observed in BJP samples. Even after the 6th PIP cycle, the density of BJP SiC samples still increased.
Figure 4.6 Density vs PIP cycle of pressed pellet and BJP SiC @ 1200 °C.

Figure 4.7 shows the cross-section microstructure of pressed and BJP SiC samples after 7 PIP cycles. In pressed SiC sample, the small volume of random open pores is observed. However, the microstructure of BJP SiC has the large volume of linear open pore channels. The longitudinal direction of pore channels is normal to the BJP direction. In our recent study, these extended defects of PIPed BJP SiC are attributed to layer-by-layer printing defects.

In traditional PIPed SiC materials, when a SiC green body is infiltrated for the first few cycles, the densities are low and pores were large and highly connected. After polymer precursor was infiltrated, the open pores space was most occupied by liquid polymer, which will crosslink during the later pyrolysis process and gradually become solid. During the pyrolysis, polymer precursor decomposes and release gas species like H₂ and CH₄, the gas species can easily escape
from the bulk material as the porosity of initial PIP cycles was still high enough. Later after more cycles, the remaining porosity is significantly smaller and it becomes gradually more difficult for the gas to escape hence the blockage of open pores start to become the majority case. Normally, after 4 PIP cycles, the local permeability of the solid phase becomes low enough that entrapped gas pockets disrupt the particle packing, causing heterogeneity in the microstructure [38].

This low-density issue of PIPed SiC ceramics gets more serious when BJ3DP is used to prepare SiC green bodies, as schematically explained in Figure 1. In binder-jetted green bodies of large SiC particles, the loosely packed region is found between each printing layer. This loosely packed region results in the microcracks in final PIPed SiC ceramics. In our recent study, more polymer precursor tends to accumulate in the interlayer region, fill it up with amorphous SiC, and lower the permeability for gas release. Accumulated gas pressure in the interlayer region eventually creates cracks, forms extended pore channels, and increases the non-uniformity of the microstructure of SiC ceramics. This locally damaged microstructure was detected on reconstructed CT cross sections.

In BJP SiC samples, open pores were much larger, and there were some linear cracks or layer-by-layer defects due to the ununiformity of powder spread during printing.
To resolve this micro-scale cracking of BJP SiC, it is important to increase the gas permeability in the interlayer region. For this purpose, not only AHPCS but also Ni nanoparticles are infiltrated to porous SiC green bodies. Since Ni and AHPCS form nickel silicide (NiSi or Ni$_2$Si), the pyrolysis above the melting temperature of nickel silicide forms the liquid phase which prevents complete blockage of pores [66]. In a current study, we examined how this liquid phase at high temperature influences the trapping and permeation of dissociated gas. Figure 4.8 shows the density and open porosity of SiC samples which is infiltrated with pure AHPCS and Ni added AHPCS. While the addition of Ni nanoparticles increased the bulk density in both pressed and BJP SiC, the effect of Ni addition becomes more obvious in BJP SiC. A preferable level of density growth rate was extended for longer cycles after transient liquid was applied to the BJP samples. The relative open porosity of BJP-SiC was decreased from 25% to 19% after 7 PIP cycles. This indicates that the shaping method has an impact on the densification of bulk SiC by PIP.

Figure 4.7 Cross-section SEM images of SiC after 7 PIP cycles (pyrolysis temperature – 1200 °C): a) pressed SiC, b) BJP SiC.
Figure 4.8 a) Density (solid lines) and open porosity (dash lines) vs PIP cycle curve of Ni effect on BJP3D and pressed SiC bulk, b) a decrease in the fraction of open porosity removed in an infiltration cycle with increasing number of PIP cycles.
The effect of additional nanoparticles also has advanced improvement in eliminating printing defects between printing layers due to the BJP technique. A microstructure of SiC cross-section was shown in Figure 4.9, which compares the non-addition SiC samples and Ni addition samples after 7 PIP cycles. In BJP SiC of pure AHPCS, the microcracks are formed and they are normal to the printing direction. Blockage of open pores increased the gas pressure in the interlayer region that eventually erupts and turns to the microscale cracks. In contrast, a mixture of Ni nanoparticles and AHPCS eliminates the extended microcracks that are formed along the interlayer region between printing layers of the BJP. Figure 4.9(b) shows most of the interlayer region is filled with amorphous SiC which is converted from AHPCS. This indicates the formation of a transient liquid phase unblock the interlayer pore channels that would have been clogged in traditional PIP process. Hence the pore channels remain open for the gas release and final SiC products have less microcracks. This explains why the additional Ni nanoparticles increase the density in 5th to 6th PIP cycles at which the microcracks appear in pure AHPCS infiltrated BJP SiC.
To examine the internal structure of PIPed SiC, micro-CT scan is performed. Figure 4.10 shows the reconstructed CT images (thresholded 2D sliced Z stack images) of three types of SiC samples: pressed SiC infiltrated with Ni nanoparticles and AHPCS, BJP SiC infiltrated with pure AHPCS, and BJP SiC infiltrated with Ni nanoparticles and AHPCS. For BJP samples, 2D slice images are taken in a plane normal to the printing direction. In each sample, 3 images are chosen to find out representative microstructures. A white and black part of the images correspond to solid and pore, respectively. BJP SiC sample of pure AHPCS has larger and winding-shape cracks. Micro-scale cracks are consistent with large pore channels found in SEM images of Figure 4.7(b) and 4.9(a). The winding-shape shape cracks are rarely observed in Ni added PIP case. This suggests that the addition of Ni nanoparticles helps to release gas from the interlayer region and prevent the eruption of accumulated gas. The melting temperature of nickel silicide phases is 980 °C and 1255 °C for NiSi and Ni$_2$Si, respectively. During high temperature pyrolysis, the melted transient liquid phase can create tiny channels which facilitate the permeation of dissociated gas, thus less cracked defects are formed.
From µCT-scan images of Figure 4.10, the pore fraction of each layer is calculated and listed in Figure 4.11. The images of entire volume are used in this calculation to estimate a change in the density of BJP SiC along the printing direction of BJP SiC samples. When pure...
AHPCS is infiltrated, the high porosity section is observed every 200~300 um that is the thickness of a single printing layer in BJP printing process. This confirms the micro-cracks are formed in the interlayer region of BJP SiC. A mixture of Ni nanoparticles and AHPCS remove this periodic porous section and make the solid fraction of each layer constant. It is consistent with SEM images of Figure 4.9(b) which exhibits more uniform microstructure of Ni-AHPCS BJP SiC.

![Pore fraction plot of different SiC samples obtained from Z-stack images.](image)

**Figure 4.11** Pore fraction plot of different SiC samples obtained from Z-stack images.

By applying different pyrolysis temperatures on PIPed samples, transient liquid formation was slightly changed. From previous study, NiSi/Ni2Si transient liquid phase have different priority under different pyrolysis temperature range. This was closely related to the melting temperature of two components [23].
It is noted that NiSi and Ni₂Si have different melting temperatures (980 °C and 1255 °C) and the amount of transient liquid phase can be increased by increasing the pyrolysis temperature [25,66]. To test the effect of an increase in the silicide liquid, pyrolysis temperatures increase from 1200 °C to 1325 °C during the 4th ~ 7th PIP cycles and the density of PIPed samples are measured. Figure 4.12 shows the temperature effect on density of BJP SiC samples. An increase in the pyrolysis temperature increases the density of SiC. When temperature increased from 1200 °C to 1325 °C, the final density after 7th cycle increased by 6% (from 78% to 84%). However, when pure AHPCS is infiltrated to BJP SiC, there is a negligible difference in the density between 1200 °C pyrolysis and 1325 °C. This difference indicates that the improvement of the density by adding Ni nanoparticles is due to the higher pyrolysis temperature that above the melting point of Ni₂Si phase. At 1325 °C, both NiSi and Ni₂Si melt and more liquid phase is available for the gas permeation and the densification. However, since 1275 °C is too low for the grain growth of pure SiC, an increase in the pyrolysis temperature from 1200 °C to 1275 °C does not change the density of pure AHPCS added BJP SiC.
4.3.2 SPS Technique on BJP-SiC Samples.

Traditional BJP method on SiC shaping have the issue that initial density was much lower than other shaping methods like uniaxial pressing or SLS technique. The main disadvantage of BJP is the printing defects that appeared repeatedly along the printing direction that will result in lower partial density inside bulk material as well as lower mechanical properties (Figure 4.10). There were multi reasons that effect the printing defects, such as particle size, powder spread speed, binder saturation and droplets size, etc. In previous sections, multi-PIP cycles with additional sintering aids Ni and carbon nanoparticles were already applied on BJP-SiC green body. As PIP process was a long and complex process, BJP-SiC sintering
process can be shortened by applying SPS step as a supplemental step of PIP, which can significantly improve the density of SiC bulk with a much faster sintering process.

In this section, the SPS process was applied on SiC bulk samples between the 4\textsuperscript{th} and 5\textsuperscript{th} PIP cycle. The electronic field-assisted LPS was performed in a DCS-10 apparatus (Thermal Technologies, Inc.) under argon atmosphere using a graphite die with diameter 10~12.7mm. The system was heated with 50 °C/min ramping rate to a maximum of 1600 °C under 75Mpa pressure environment. Samples after sintering were automatically cooled down in argon ambiance until room temperature. The samples after SPS were then treated with 3 more PIP cycles as a control of variability. By comparing bulk density, open/close porosity, and microstructure in cross-section of both SPS-PIP applied samples and PIPed SiC ceramic samples, the effect of SPS process was listed in Table 3.
Table 3 SPS and PIP method on BJP-SiC green body

<table>
<thead>
<tr>
<th>Technique</th>
<th>No Ni case</th>
<th>With Ni case</th>
</tr>
</thead>
<tbody>
<tr>
<td>Only PIP process</td>
<td>Density slightly increase, no close pores, density slope decreased after 4th PIP cycle but still remain half of initial slope. Density reached to 77~78% of theoretical SiC crystal after 7 PIP cycles.</td>
<td>Density slope was higher than no Ni case, also show much greater improvement with 1275 C sintering than 1200 C sintering. Density reached to 82~83% of theoretical SiC crystal after 7 PIP cycles.</td>
</tr>
<tr>
<td>SPS applied process</td>
<td>By apply SPS process on SiC sample after 4 PIP cycles, density quickly increased from 69% to 76%. However, high pressure SPS result in large cracks on SiC bulk due to printing defects from BJP technique. Also close porosity was increase from 0 to around 4%. The PIP cycles after SPS only help filling the cracks with PDCs, meanwhile didn’t show much improvement in bulk density.</td>
<td>While Ni was added in both initial PIP cycles and afterwards PIP cycles, the bulk density slightly increased as expected, the SPS process applied after 4 PIP showed great improvement on SiC bulk density which was increased from 73% to 80%, smaller cracks was observed due to high pressure. Although the afterwards PIP cycles showed very little improvement on bulk density, NiSi liquid phases help fill the cracks and decrease rate of close pores by unblock closed pores.</td>
</tr>
</tbody>
</table>

Figure 4.13 shows the density curves of both SPS applied samples and PIPed SiC samples. The solid lines express the change of relative bulk density, while dash lines refer to close porosity of SiC samples. The sudden improvement in density curves referred to the improvement of SPS applied on SiC samples after the 4th PIP cycle. The density of SPSed SiC ceramic sample is even higher than PIPed samples after 7th PIP cycle, which was considered over the limitation of traditional PIP process on the density growth. The SPS process also created a sudden appearance of close pores, as the close porosity showed a rapid increase from around 0.5% to 5% of total volume. By applying more PIP cycles after SPS process, density of SiC samples didn’t have much change, corresponding to the density limitation of PIP technique [22]. The formation of large number of close pores was considered to have direct relation with high pressure during SPS sintering. It was also considered that the high pressure applied on relative
porous SiC bulk samples during SPS will result in cracks along the printing defects layers as well as the formation of close porosity.

![Graph showing density and close porosity vs PIP cycle curves of SPS applied BJP-SiC bulk samples.](image)

**Figure 4.13** Density and close porosity vs PIP cycle curves of SPS applied BJP-SiC bulk samples.

On the other side, the result from SPS samples also provide evidence for the effect of Ni nanoparticles in PIP technique. Regardless of density improvement of SiC bulk samples, Ni nanoparticles also stave off the formation of close pores from PIP process. In traditional PIP process of BJP-SiC samples, close pores formed after few cycles of infiltration and then formed cracks due to gas releasing [38]. The printing defects between layers boost this issue and create crack layers which can be observed from CT images or SAF curves (Figure 4.1,4.9, 4.10). By applying additional Ni nanoparticles in PIP process, the formation of low melting point liquid
phases – NiSi and Ni$_2$Si – help the unblockage of open pores and prevent the crack formation that would have been created by gas releasing. The close porosity curve in Figure 4.13 clearly proved the effect of Ni nanoparticles after high close porosity that was already made by SPS technique, while the close porosity gradually decreased during 5~7$^\text{th}$ PIP cycles were applied after SPS step.

Figure 4.14 Microstructure of BJP-SiC samples after 1~4$^\text{th}$ PIP cycles with Ni addition and SPS process, (a)surface microstructure; (b) cross-section image of sample after SPS process; (c) after additional 5~7$^\text{th}$ PIP cycles with Ni addition.
Figure 4.14(a) presents the SEM images of SPSed samples surface, while the large cracks were observed in bulk sample surface. After a few more Ni-PIPed cycles after SPS step, cracks were filled with PDCs, and closed pores were re-opened. The microstructure of cross-sections between individual SiC crystal particles were clearly shown in Figure 4.14(b)(c), to present the effect of Ni added PIP process in the help of density uniformity. Red circles were individual SiC particles, while yellow circles were PDC filled areas, which were relative porous after SPS process, but then filled with afterwards PIP process with Ni addition and become fully dense.

4.4 Conclusion

In this chapter, SiC samples were successfully printed by ExOne innovent and 400-mesh α-SiC as raw material. The SiC green body were pre-sintered at 1500 °C and further consolidated via polymer infiltration and pyrolysis for a maximum of 7 cycles with 1200~1325 °C. Powder characteristics and microstructure evolution during PIP processing were investigated using SEM and 2D-µCT characterization techniques. An advanced PIP method was applied on BJP SiC samples in this study and clearly shows an improvement compared with normal PIP.

The improvement of advanced PIP method on BJP SiC samples is similar as the result of uniaxial pressed SiC samples in chapter 2. The advanced PIP method introduced the additional Ni nanoparticles to form a transient liquid phase. The formation of NiSi/Ni$_2$Si transient liquid phase has been proved to have a positive effect on unblockage of open pores and thus help improve the infiltration and pyrolysis efficiency of SiC bulk samples. By comparing microstructure and 2D SAF results between non addition and Ni addition samples, the latter one shows less porosity and a higher filling state on large pore channels which is caused by layer-by-
layer 3D printing. It was also found that the infiltration efficiency of beginning PIP cycles was improved by adding Ni nanoparticles. As the sintering efficiency slowed down after 4th PIP cycle, an additional SPS step was applied and fasten the sintering of SiC bulk which result in even higher density than 7 cycle PIPed samples. This gives some idea to solve the disadvantage of long PIP process during high density samples manufacturing. Generally, Ni added PIP method improve the overall density of BJP SIC samples, as well as a considerable elimination of printing defects from BJP technique.
Chapter 5 Overall Conclusion

In this study, SiC green body was produced with both uniaxial pressing and BJ3DP method to provide different initial density green body materials. By applying traditional polymer infiltration and pyrolysis (PIP) on SiC densification and developing an advanced PIP method with additives including Ni and carbon nanoparticles to further enhance the density of final products. The step-by-step PIP method provided a controllable sintering process with alternative temperature, additives in polymer, infiltration pressure, and number of PIP cycle. The advanced PIP method with additives has been applied on both pressed and BJP-SiC green bodies and presented excellent improvement in density and porosity compared with traditional PIP method. The chemical analysis on reactions between SiC and additives during sintering process showed the presence and removal of transient liquid phase NiSi and Ni$_2$Si, which were also believed to have an important role in pore unblockage. The explorer in temperature effect provides evidence on the effect of liquid phase in bulk density enhancement after sintering. The advanced PIP method partially resolves the disadvantage of traditional PIP method on the density limitation due to blockage of open pores. The small but positive slope of SiC density curves present the fact that much higher relative density (>93%) can be reached on SiC bulks with this advanced PIP method.

Additional study on producing higher purity SiC bulk samples and shorten the process of PIP sintering method was applied on both pressed and BJP-SiC green body samples. Carbon nanoparticles was introduced into latter PIP cycles as a reduction additives to reduced the amount of transient liquid phase NiSi and Ni$_2$Si, by applying extra amount of carbon sources, nickel silicide phases was gradually reduced and finally reached to a low level. During these PIP cycles, the effect of transient liquid phase gradually decreased and close pores formed.
correspondingly. However, the bulk density has already reached a high level at this time as expected. The use of SPS sintering step during middle section of multi-PIP cycles also showed significant improvement in the density of SiC samples. One step of SPS process showed similar or even higher efficiency than 3 PIP cycles. However, the use of high heating rate and high pressure bring negative effect on close porosity and physical breaking of SiC bulk. These disadvantages will be one of the future works to solve.
Bibliography


[20] Rujie He, Guojiao Ding, Keqiang Zhang, Ying Li, Daining Fang, Fabrication of SiC ceramic architectures using stereolithography combined with precursor infiltration and pyrolysis, Ceramics International, Volume 45, Issue 11, 2019, Pages 14006-14014, ISSN 0272-8842.


