Effect of Nitrogen Dopant on Electrical Resistance of Hot Zone of SiC Heating Elements

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Abstract. In the present work gaseous nitrogen is used as dopant in silicon carbide heating element to study the effect of electrical resistance in heat generation portion of heating elements. The silicon carbide heating elements are used mainly in non-ferrous alloy melting and holding furnaces in automotive and aerospace industrial applications. The gaseous nitrogen plays a major role as dopant in achieving the electrical resistance of SiC heating elements. The green silicon carbide is used to prepare the heating element by powder metallurgy process because of its high mechanical strength, resistance to corrosion, and high thermal conductivity at elevated temperature. However, the nitrogen acts as dopant in silicon carbide to achieve the electrical resistivity in the heating element to generate uniform heat in hot zone portion of SiC heating elements while sintering. The hot zone of SiC heating element is connected with cold zone at both the terminals of heating element to pass the current to hot zone to generate the heat by its higher resistivity. A range of nitrogen gas flow rate ranges from 76 lt/hr to 84 lt/hr with 99.99% purity of industrial grade passed to the sintering furnace, in turn it acts as dopant and creates inert atmosphere in the sintering furnace, then the SiC heating element tubes were made and analysed. The results indicate that the quantity of gaseous nitrogen dopant influenced the electrical resistivity of the heat generating portion of SiC heating element.

1. Introduction
Silicon carbide has numerous industrial applications such as heating elements, automobile brake pads, semiconductors, etc.. The electrical and mechanical properties of SiC are known to vary over large ranges depending on methods of manufacture, dopants and their mass fractions, and post treatment (such as siliconizing). Dopants can be solids such as Aluminium, Boron, Iron, etc., or gases such as Nitrogen. Methods of manufacture usually involve mixing of core ingredients, pressing, drying, sintering, and post treatment.

Methods of manufacture and resultant material properties of SiC are under continuing international study. Industrially produced SiC is referred to as Carborundum and crystolon [1]-[3]. β to α transition occurs rapidly at around 2300°C. High nitrogen pressures favour the reverse process [1]-[5]. Normal transformation of SiC is from cubic (3C) to hexagonal (6H) [6]. The atmospheric pressure difference between concave and convex surfaces of SiC particles can be of the order of $10^6$ to $10^5$ atmospheres [7]-[9]. Grain size was found to be dependent on isostatic pressing temperatures [10].
An improved production with low energy consumption is reported [11]. Use of boron as dopant with improved properties is reported [12]. Phase transitions between 3C-6H have been studied [1-12]. Effects of aluminium and zinc have been studied [13]. A method of tuning the electrical properties is reported [14]. A CVD formed SiC product [15]. Explosive compaction is investigated [16]. Impregnation with acid and coating with oxides, enamels, or glass to protect against oxidation has been investigated [17]. Effect of boron has been investigated. Efficient methods of production are investigated [18]. Doping with nitrogen (N2) has been investigated [19]. a method for imparting high insulation property and corrosion resistance. An improved production method is reported in. Additional variations are reported in [20][21] investigates doping by aluminium, additional carbon, oxygen, and nitrogen. A method to prepare wear and corrosion resistant SiC is reported, the preparation of SiC conjugate [22],[23].

2. Methodology
The following steps are followed for preparing samples;
1. Selection of SiC raw material grit size.
2. Preparing Ingredients and Blending: Mixing of SiC powder weight ratio along with binder and water to make lumps for pressing.
3. Extrusion: Prepared lumps pressed through horizontal cold extrusion to make samples.
4. Drying: Extruded samples are dried in the oven to remove moisture in the green samples.
5. Sintering: Dried samples passing through continuous carbon tube furnace to sinter the samples along with gaseous nitrogen inert atmosphere.
6. Testing: Sintered samples are tested for its electrical resistance.
7. Results and discussion: experimental results are discussed.

![Flow chart showing heat generating zone of SiC heating elements.](image-url)
3. Experimentation

3.1. Selection of SiC powder and blending
SiC powder with 99% purity in the form of green silicon carbide. The proportion of green SiC grit size of 24 # to #36 granularity from 5% to 10% of coarse grains, The grit size 80 # to 90 # of medium grains 45% to 50%, and the grit size in the form of fine grains 1000# to 1200 # of weight 30% to 40%. The methylcellulose as binder, range of viscosity 3500-5600 mPa. s (at 20 ° C, 2%), methoxy content 27% to 30%. The ingredients are mixed in a muller mixing machine for about 45 to 55 minutes, upon lumps formation after adding required quantity of water. Figure 2 shows the schematic process flow of SiC heating element tubes.

![Figure 2](image-url)  
**Figure 2.** Process of hot zone portion of SiC heating elements tubes.

3.2. Extrusion
Lumps formed in the mixing machine is pressed in the extrusion to form tube of required diameter. Weigh 24 # 1500 grams of green silicon carbide, 1200 # 3000 grams, 300 # 1000 grams, 80 # 4500 grams, 420 #1750 grams, mixed for 15 minutes then added methyl cellulose of 2% with water of 8% to 9%. Mixing was continued upto 45 minutes to form lumps and then pressed at 85 Mpa to 95 Mpa to form tube of Ø25mm.

3.3. Drying
Formed tubes were dried at 20 ~ 40 °C for 24 hours at ambient temperature, then raised temperature to 180 ~ 200 °C for 3 hours.

3.4. Sintering
The dried SiC tubes were pushed through continuous tube furnace for sintering. Gaseous nitrogen dopants are introduced in the furnace to make inert atmosphere. A schematic arrangement of the sintering furnace is shown figure 3. The sintering furnace consists of pre-heat zone temperature 350° C-800° C, sintering zone temperature of 2450° C - 2550 °C, carbon tube length 2000 mm, and cooling zone, advanced by constant pusher ramp rate, under variable gaseous nitrogen flow of 99.99% purity (industrial grade) from 76 lt/hr to 84lt/hr.
Figure 3. A schematic of the arrangement of sintering process.

Time spent in each of the zones is determined by the rate at which the product is being moved through the system (pusher rate). This is one of the parameters which can be chosen to help achieve the desired property for the finished product.

3.5. Testing
Sintered SiC heating elements tubes are tested for its electrical resistance by maintaining constant voltage. Samples of Ø25mm, length 500mm SiC tube has been produced at constant push rate and temperature process parameters with variable gaseous nitrogen flow from 76 lt/hr to 84lt/hr.

Figure 4 shows the uniform heat generation of hot zone of SiC heating elements.
After sintering, SiC heating tubes resistance has been measured and uniform glow of hot zone portion of heating elements has been observed as tabulated below in table 1 to 5. For measuring each SiC heating element tube resistance, the constant voltage maintained to note the current readings in amperes, the current and voltage indicates the electrical resistivity of sintered SiC heating element tubes. The resistance of the SiC tubes based on current flow and its porosity, sintering of SiC grains, nitrogen dopant.

Table 1. Hot Zone Ø25mm, length 500mm, constant pusher speed 20mm/min at Nitrogen gas flow rate 76 lt/hr & furnace temperature 2400°C.

| Sample | Voltage (V) | Current (A) | Resistance (Ω) |
|--------|-------------|-------------|----------------|
| 1      | 55          | 56.04       | 0.981          |
| 2      | 55          | 52.01       | 1.057          |
| 3      | 55          | 50.06       | 1.098          |
| 4      | 55          | 53.00       | 1.037          |
| 5      | 55          | 49.11       | 1.119          |
| 6      | 55          | 52.18       | 1.054          |
| 7      | 55          | 48.10       | 1.143          |
| 8      | 55          | 48.55       | 1.132          |

Table 2. Hot Zone Ø25mm, length 500mm, constant pusher speed 20mm/min at Nitrogen gas flow rate 78 lt/hr & furnace temperature 2400°C.

| Sample | Voltage (V) | Current (A) | Resistance (Ω) |
|--------|-------------|-------------|----------------|
| 1      | 55          | 65.12       | 0.844          |
| 2      | 55          | 69.3        | 0.793          |
| 3      | 55          | 68.43       | 0.803          |
| 4      | 55          | 65.53       | 0.839          |
| 5      | 55          | 66.8        | 0.823          |
| 6      | 55          | 65.93       | 0.834          |
| 7      | 55          | 64.95       | 0.846          |
| 8      | 55          | 67.15       | 0.819          |

Table 3. Ø25mm Hot Zone length 500mm, constant pusher speed 20mm/min at Nitrogen gas flow rate 80 lt/hr & furnace temperature 2400°C.

| Sample | Voltage (V) | Current (A) | Resistance (Ω) |
|--------|-------------|-------------|----------------|
| 1      | 55          | 77.04       | 0.713          |
| 2      | 55          | 79.36       | 0.693          |
| 3      | 55          | 76.42       | 0.719          |
| 4      | 55          | 78.65       | 0.699          |

Table 4. Hot Zone Ø25mm, length 500mm, constant pusher speed 20mm/min at Nitrogen gas flow rate 82 lt/hr & furnace temperature 2400°C.

| Sample | Voltage (V) | Current (A) | Resistance (Ω) |
|--------|-------------|-------------|----------------|
| 1      | 55          | 83.23       | 0.660          |
| 2      | 55          | 83.96       | 0.655          |
| 3      | 55          | 84.3        | 0.652          |
| 4      | 55          | 83.51       | 0.658          |
Table 5. Hot Zone Ø25mm, length 500mm, constant pusher speed 20mm/min at Nitrogen gas flow rate 84 lt/hr & furnace temperature 2400°C.

| Sample | Voltage (V) | Current (A) | Resistance (Ω) |
|--------|-------------|-------------|----------------|
| 1      | 55          | 85.23       | 0.645          |
| 2      | 55          | 86.96       | 0.632          |
| 3      | 55          | 87.38       | 0.629          |
| 4      | 55          | 85.51       | 0.643          |
| 5      | 55          | 88.16       | 0.623          |
| 6      | 55          | 86.21       | 0.637          |
| 7      | 55          | 85.73       | 0.641          |
| 8      | 55          | 86.75       | 0.634          |

4. Results and discussion
In order to investigate the effects of gaseous nitrogen dopant on hot zone portion of SiC heating element tube, a continuous carbon tube furnace was used. By varying the nitrogen gas flow rate through the furnace, the sintering time kept constant by maintaining the push ramp rate. Higher the nitrogen gas flow rate, the lesser the resistivity in the sintered SiC heating elements and uniform red hot eveness in the element.

Table 6. Dia 25mm Hot Zone, length 500mm, variable nitrogen gas flow rate 76 lt/hr to 84 lt/hr at furnace temperature 2400° C, Resistance in Ohm (Ω).cm.

| Temp. in °C | Nitrogen Flow Rate |
|-------------|--------------------|
|             | 76 lt/hr | 78 lt/hr | 80 lt/hr | 82 lt/hr | 84 lt/hr |
| 30          | 0.0291   | 0.0232   | 0.0194   | 0.0165   | 0.0159   |
| 200         | 0.0265   | 0.0213   | 0.0175   | 0.0162   | 0.0153   |
| 400         | 0.0253   | 0.0192   | 0.0165   | 0.0146   | 0.0142   |
| 600         | 0.0241   | 0.0176   | 0.0143   | 0.0138   | 0.0137   |
| 800         | 0.022    | 0.0165   | 0.0137   | 0.0132   | 0.0126   |
| 900         | 0.02     | 0.0159   | 0.0128   | 0.0129   | 0.0118   |

From the table 1 to 6, the resistivity of SiC heating elements tubes for a overall length of 500mm heat generation portion of various test samples by varying nitrogen flow rate at temperature 900 °C as noted in table 6. Temperature in °C and resistivity Ohm per cm as tabulated in table 6 of sintered SiC heating elements passed through the continuous carbon tube
furnace by varied nitrogen flow rate as explained in the results and discussion. The electrical resistivity of the SiC hot zone material sintered at varied nitrogen flow rate ranges from 76 lt/hr to 84 lt/hr at a furnace temperature of 2400°C with +/- 10°C with push ramp rate of 20mm/min.

Figure 5 shows graph of resistivity v/s temperature for heat generating portion of SiC heating element tubes extruded from SiC of constant grain size formed through a continuous carbon tube furnace at different nitrogen flow rate.

The electrical resistivity of the hot zone green silicon carbide material sintered at different nitrogen flow rate from 76 lt/hr to 84 lt/hr at a constant sintering furnace temperature range of 2400-2450°C. A nitrogen flow rate of 76 lt/hr possesses maximum resistivity. Figure 5 shows a graph of resistivity of hot zone of heating portion versus temperature when sintered at various nitrogen flow rate. The reduced electrical resistivity achieved by increasing the nitrogen gas flow rate from 82 lt/hr to 84 lt/hr is nominal when the gas flow rate is reduced from 78 lt/hr to 76 lt/hr. Although the nitrogen gas flow rate of 84 lt/hr showed the highest reduction in electrical resistivity, such a high nitrogen gas flow rate increases the cost of production. With the particular furnace used, the nitrogen gas flow rate of 82 lt/hr was considered optimum.

![Figure 5. Resistivity versus temperature at different nitrogen flow rates for hot zone.](image)

**Figure 5.** Resistivity versus temperature at different nitrogen flow rates for hot zone.

**Conclusions**
In this work, the processing of heat generating portion of SiC heating elements can be optimized by controlling the gaseous nitrogen flow in the sintering furnace to maintain inert atmosphere and as dopant in the sintered SiC heat generation portion, it has the advantage in stability of high resistivity value, performance, and improved yield of sintered hot zone of SiC heating element.

However, it has been found that the influence of nitrogen gas makes inert atmosphere in the sintering furnace and act as dopant in the sintered SiC hot zone of heating element reduces the resistivity of the hot zone of SiC heating element.

SiC Sintered temperature at 2400°C in optimum nitrogen gas flow rate (84 lt/hr) prominently reduced the resistivity (0.0126 Ω.cm at 800°C) when compared with nitrogen gas flow rate of 76 lt/hr. From this observed that nitrogen is doped in the SiC lattice while sintering in nitrogen inert atmosphere in the continuous carbon tube furnace, which transformed the β-SiC to α-SiC.
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