氮化硅陶瓷
Silicon Nitride Ceramics

www.visit-silicon.com

Introduction

- The contents of nitrogen and silicon on the earth are very high.
- The content of nitrogen in the air is about 78.6%.
- Silicon is the element with the content only second to oxygen in the crust. (26.09%)
- There is no compound of nitrogen and silicon in nature.
- Silicon nitride is a new synthetic materials (1857)

$$3Si + 4NH_3 \rightarrow Si_3N_4 + 6H_2$$

In the 1880s, people had prepared the silicon nitride bulk material.

Introduction

- After World War II, science and technology developed rapidly, and the high-tech fields such as atomic energy, rockets, gas turbines put forward higher requirements on the materials,
- Forcing people to seek the new material that can better withstand high temperatures than the heat-resistant alloy and can be more resistant to chemical corrosion than ordinary ceramic.
- The excellent performance of silicon nitride ceramics inspired the enthusiasm and interest of people in it.

Introduction

- High strength at room temperature and high temperature
- High hardness
- Good abrasion resistance
- High oxidation resistance
- Favorable resistance to thermal and mechanical shock
- In the field of high-temperature structural ceramics, silicon nitride ceramic is a new material with the best overall performance and the most potential applications, the most promising alternative to nickel-based alloys and widely used in high-temperature areas.

Structure of Silicon Nitride

- Silicon nitride is connected by the covalent bond with nitrogen and silicon. The structure is complex, generally including
- β-Si_3N_4, the space group: P63/m; the hexagonal lattice constants: a = 0.7608nm, c = 0.2910nm; easy to form the long columnar structure
- α-Si_3N_4, the space group: P31c; the hexagonal lattice constants: a = 0.7748 ~ 0.7765nm, c = 0.5617 ~ 0.5622nm; easy to form the equiaxed grain structure

Structure of Silicon Nitride

- Heated at 1400~1600℃, α-Si_3N_4 will be converted into β-Si_3N_4, but we cannot say that α-phase is the low temperature crystal while β is the high-temperature crystal type.
- Both phases can exist in the synthesis at low temperatures.
- Except for the degree of symmetry, the two structures have no differences on high and low temperatures. Just α-phase has lower symmetry, easy to form, and β-phase is thermodynamically more stable.

Physical and Chemical Properties of Silicon Nitride

- Thermal property: a high-temperature refractory compound

  No melting point, decomposed at atmospheric pressure at about 1900 ℃,

  High temperature creep resistance, the binder-free reaction-sintered silicon nitride has the load softening point up to 1800 ℃.
- Small thermal expansion coefficient, (2.8 ~ 3.2) × 10-6 / ℃
- Good thermal conductivity - (2 ~ 155W / (mK))

  - Good thermal shock resistance (The thermal shock from room temperature to 1000 ℃ will not lead to crack.)

Physical and Chemical Properties of Silicon Nitride

- Electric Insulating Property (electrical resistivity: $10^{15}\sim10^{16}\Omega$ cm)

  Low dielectric loss, high resistance to breakdown voltage

  (Affected by the synthesis methods, free Si, the impurities introduced in sintering aids, etc.)
- Chemical stability: Silicon-nitrogen covalent bond, high bond energy, high enthalpies of formation - a stable compound

(1.) oxidation resistance

Below 800 ℃, no reaction with oxygen in the dry atmosphere

Physical and Chemical Properties of Silicon Nitride

- Over 800 ℃, the reaction starts.

$$Si_3N_4 + 3O_2 \rightarrow 3SiO_2 + 2N_2$$

- During the reaction, the silicon oxide film will be generated on the surface of the sample, and the silicon oxide film gradually becomes stable with increasing temperatures.
- Up to about 1000 ℃, it will form a dense silicon oxide protective layer to prevent further oxidation of the silicon nitride. Until 1400 ℃, all are basically stable.

Physical and Chemical Properties of Silicon Nitride

- In the humid air, when the silicon nitride is heated above 200 ℃, the surface oxidation can immediately occur.

$$Si_3N_4 + 6H_2O \rightarrow 3SiO_2 + 4NH_3$$

- The silicon oxide produced by this reaction is amorphous and can not form a dense protective film, so the reaction will continue to proceed slowly.
- In addition, the oxidation has a lot to do with the pores of silicon nitride ceramics and the grain boundary phase formed by the additives. Alkaline metal impurities will speed up the oxidation reaction.
- Uneven portions and impurities will accelerate local oxidation, form pits, and greatly reduce the strength of the ceramic.

Physical and Chemical Properties of Silicon Nitride

- Resistance to Corrosion of Molten Metal

Silicon nitride is free from infiltration or corrosion of molten elemental metals (Al, Zn, Cd, Au, Ag, Sn, Pb, Bi, Ga, Ge, In).

In vacuum or the inert gas, it is free from the corrosion of Cu. In the presence of oxygen, copper oxide will react with silicon nitride.

Mg and Si can make silicon nitride wet and slightly eroded.

The molten transition elements can strongly wet silicon nitride and react with Si to generate a silicide, and rapidly decompose the silicon nitride to release nitrogen.

Physical and Chemical Properties of Silicon Nitride

- For the molten alloy
- Silicon nitride is very stable to brass, hard aluminum, and nickel silver, etc., , also has good corrosion resistance to cast iron, and carbon steel, etc., but has no resistance to corrosion of nickel-chromium alloy, and stainless steel, etc.

- (3.) Resistance to acid-bases and salts
- General acid-bases have no effect on silicon nitride (HCl, concentrated nitric acid, aqua regia, phosphoric acid, sulfuric acid below 85% with temperature less than 80 ℃, and NaOH solution below 25%).

Physical and Chemical Properties of Silicon Nitride

- Hydrofluoric acid has obvious corrosion on the silicon nitride.
- The molten alkali and salts such as molten NaOH have obvious corrosion on the silicon nitride.
- The nature of the grain boundary has a great impact on the corrosion resistance.
- Also stable for the strong radiation.

Mechanical Properties of Silicon Nitride

- Hardness

α-Si_3N_4—HV (15～20Gpa)

β-Si_3N_4—HV (32～34Gpa) (5 to 10 micrometers for indentation)

The Mohs hardness is only after silicon carbide, boron carbide, cubic boron nitride and diamond.

Mechanical Properties of Silicon Nitride

- Coefficient of Friction and Self Lubrication
- The coefficient of friction is low, and under the conditions of high temperatures and high speed, the increased rate is also smaller, so this can ensure the normal operation of mechanism.
- The silicon nitride ceramic has self lubrication.
- ---Under pressure, the thin air film can be formed by trace amount of decomposition on the friction surface, so that the sliding resistance between the friction surfaces will be reduced, and the amount of wear will be very small.

Mechanical Properties of Silicon Nitride

- Mechanical Strength

  With the differences of preparation processes and organizational structures, there will be a more substantial change. The flexural strength is within the range of 100 ~ 1200Mpa.

- Fracture Toughness

  Relatively high (3～9Mpa $\cdot m^{1/2}$) tetragonal zirconia up to 15, cast iron and hard alloy (～30), higher than aluminum oxide and silicon carbide

- The high-temperature intensity depends on the grain boundary phase.

Mechanical Properties of Silicon Nitride

- Machinability

  Unsintered high-pressure isostatic billet (such as pressure 600Mpa) can be directly machined.

  Semi-sintered green sheets can be processed by the center lathe, and then fully sintered.

  Sintered ceramic can be sliced by the diamond wheel, and can also be precisely milled. The surface roughness can reach up to 0.025 microns (mirror-like glossy surface); 0.006 microns (mirror)

Manufacturing Methods of Silicon Nitride Ceramics

- Generation Method of Raw Material Powder
- 1). Direct Nitridation of Silicon Powder

$$3Si + 2N_2 \xrightarrow{1200℃\sim1450℃} Si_3N_4$$

$$3Si + 4NH_3 \xrightarrow{1200℃\sim1450℃} Si_3N_4 + 6H_2$$

- Low temperature can easily generate high α-phase product, while high temperature will generate the β-phase product. The presence of iron can promote the reaction.
- It is an exothermic reaction, so the control of temperature should be noted in order to avoid exceeding the silicon melting point and hinder the reaction.

Manufacturing Methods of Silicon Nitride Ceramics

- 2). Ruduction and Nitridation of Silicon Oxide

$$3SiO_2 + 2N_2 + 6C \xrightarrow{1500℃} Si_3N_4 + 6CO\uparrow$$

In the production, an excessive amount of carbon and silicon oxide will introduce impurities.

- 3). Gas-Phase Synthesis

$$3SiCl_4 + 16NH_3 \xrightarrow{1400℃} Si_3N_4 + 12NH_4Cl$$

$$3SiH_4 + 4NH_3 \xrightarrow{1400℃} Si_3N_4 + 12H_2\uparrow$$

High-purity and ultrafine silicon nitride powder can be obtained.

Manufacturing Methods of Silicon Nitride Ceramics

- 4). SHS (self-propagating reaction synthesis)

$$3Si + 2N_2(\text{高压}3\sim10Mpa) \xrightarrow{\text{点火自蔓延燃烧}} Si_3N_4$$

- The self-propagating silicon powder usually has high β content. The approach to increase the content of α-phase is to add α-phase powder into the silicon powder as the seed crystal and to reduce the combustion temperature (adding diluents), etc.

氮化硅陶瓷的制造方法

- 氮化硅粉体成型和生坯处理

氮化硅粉和单质硅粉都属于瘠性粉体，在成型前需加成型助剂，使其利于粘合、塑化或悬浮。

所有陶瓷成型方法都可用于氮化硅的成型。

成型后的生坯中往往含有不同含量的成型剂等有机物，一般需脱胶（排蜡）工序。

脱蜡过程要特别注意升温速率，保证有机物缓慢气（液）化排出，防止生坯膨胀开裂！

Manufacturing Methods of Silicon Nitride Ceramics

- Molding of Silicon Nitride Powder and Processing of Green Body
- Silicon nitride powder and elemental silicon powder are all barren powders. Before molding, forming additives need to be added to make it conducive to bonding, plasticizing or suspending.

  All ceramic molding methods can be used for molding of silicon nitride.

  The molded green body often contains different amounts of organic matter such as forming agent, and it generally takes degumming (dewaxing) step.

  The dewaxing process should pay special attention to the heating rate to ensure organic matter slowly discharged by gasification (liquefaction) and to prevent the green body swelling and cracking.

Manufacturing Methods of Silicon Nitride Ceramics

- Sintering of Silicon Nitride
- As a high-performance material, silicon nitride ceramic must guarantee the reliability of products, so its performance must be as stable as possible!
- 1). During molding and sintering processes, try to prevent thermal stress and mechanical stress from concentration.
- 2). Reduce the defects in the ceramic body and prevent unsynchronized sintering.
- 3). The crystal grain of sintered ceramic should be fine; try to minimize the grain boundary phase as possible. The bulk density should be as close to the theoretical density as possible; lower the porosity.

Manufacturing Methods of Silicon Nitride Ceramics

- Silicon nitride is a covalent bond compound, difficult for dense sintering!

1）Reaction Sintered and Reaction Bonded Silicon nitride

Is a method of manufacturing silicon nitride ceramics first used in industrial production

Molding of silicon powder and the mixture of silicon powder and silicon nitride powder

Pre-nitriding in nitrogen at 1200 ℃

Mechanically processed into Required parts

Final nitride sintering in the nitrogen atmosphere at 1400 ~ 1500 ℃

Manufacturing Methods of Silicon Nitride Ceramics

- The molded body of Si powder generally has the porosity of 30% to 50%. After nitriding of Si powder, there is an volume increment of 22%, so the sintered green body remains basically unchanged in the shape and size.
- The process characteristic that the size remains basically unchanged after sintering by pre-nitriding and machining, can be used to manufacture the parts with precise size and complex shape, which is a notable feature different from the gas ceramic sintering.

Manufacturing Methods of Silicon Nitride Ceramics

- Reaction sintering should control the reaction rate, so the nitriding period is relatively long (generally 4-6 days).
- The sintered compact usually has the porosity of 30% and 15%, and residual silicon of 1 to 5%, and therefore the strength is generally low!
- Reaction sintering needs nitrogen gas penetrated into the internal green body, so the products of thick size (over 10 mm) is difficult to be fully nitrided, with poor performance.
- Advantages: very little decrease of the strength at high temperatures, high dimensional accuracy; less investment in equipment, relatively inexpensive product processing, suitable for mass production.

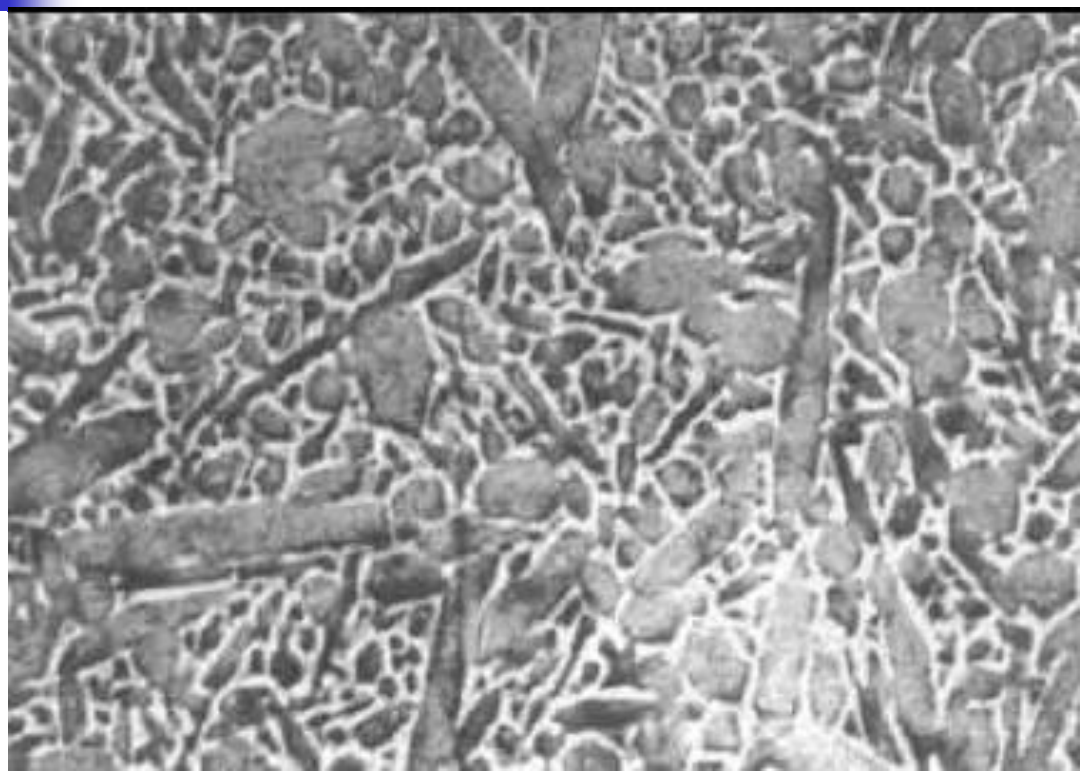
Manufacturing Methods of Silicon Nitride Ceramics

- **Hot-Press Sintering**
- **Under pressure, the applied pressure can force the material to move and achieve densification.**
- **The pure silicon nitride powder can not be densified even by hot pressing!**
- **---Adding sintering aids**
- **Sintering aids can react with the impurities of silicon nitride and silicon nitride itself to produce the glass phase boundary. The glass phase melts at high temperatures, under the action of the applied pressure, to jointly promote densification of the green body.**
- **MgO, Y_2O_3, and Al_2O_3, etc.**

Manufacturing Methods of Silicon Nitride Ceramics

- **Hot press sintered silicon nitride ceramics have high density as well as high strength (800 ~ 1200Mpa).**
- **During sintering, the α-phase may dissolve in the glass phase and precipitate the β-phase with a higher thermal stability,**
- **and under pressure, the β-phase can develop into the long columnar interwoven structure, so the fracture toughness of sintered body is also higher.**

Manufacturing Methods of Silicon Nitride Ceramics

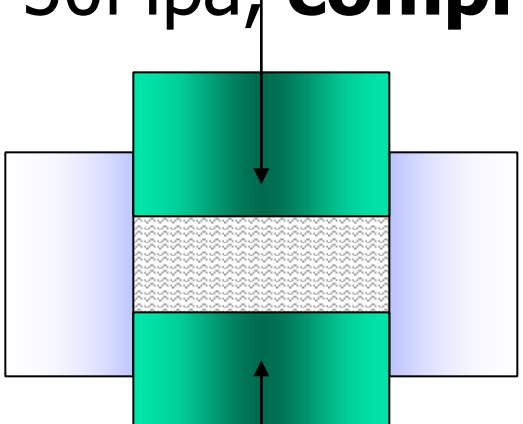


Manufacturing Methods of Silicon Nitride Ceramics

- **Hot press sintering does not require pre-forming, so the forming agent needn't to be added.**
- **The most critical of the hot pressing is the hot pressing mold (sintering at 1700 ~ 1800 ℃)**
- **Graphite mold has low intensity, in order to ensure the pressure during hot pressing, the thickness of the female mold needed to be higher as the size of hot pressing sample increases!**
- **The graphite expensive of large size and high strength is expensive, and cannot guarantee that fracture will not occur during the using process.**

Manufacturing Methods of Silicon Nitride Ceramics

- **With the use of carbon fiber composite material, the performance of dimensional pressing mold has improved a lot---reducing the wall thickness and greatly improving the safety factor.**
- **Tensile strength of carbon fiber:** 2000～3000Mpa
- **Flexural strength of high-strength graphite:** 30～50Mpa, **compressive strength** <80Mpa



Hot Pressure is generally 20～30Mpa

Hot press sintering has low efficiency, single shapes of products, and higher cost.

Manufacturing Methods of Silicon Nitride Ceramics

- **Pressureless Sintering**
- **Similar to hot press sintering, sintering additives should be added (higher addition amount than hot pressing)**
- **Raw powder must have high α content. Sintering mechanism is also the liquid phase sintering, mutually dissolving, and the precipitation process also exists.**
- **Since the high-temperature silicon nitride is easily decomposed, it is necessary to use buried powder (silicon nitride + BN + MgO) during sintering.**

Manufacturing Methods of Silicon Nitride Ceramics

- **Re-sintering (Post-Sintering)**
- **Combining reaction sintering with pressureless sintering**
- **Before sintering, put sintering additives mixed with raw material powder**
- **Put the reaction sintered compact re-sintered at high temperatures and the dense silicon nitride products can be obtained.**
- **Re-sintering must be at high nitrogen pressure (tens to hundreds of atmospheric pressure)**

Strength of products can achieve the effect of hot pressing.

Manufacturing Methods of Silicon Nitride Ceramics

- **Gas-Pressure Sintering**
- **Similar to re-sintering, but it does not require the previous reaction sintering process. The sintering temperature can reach up to 2000 ℃.**
- **Gas-pressure sintering can use pressureless sintering for 50% or less of sintering aids to achieve sintering, and the products have better performance.**
- **The main contribution of densification is from the higher temperatures, and the high nitrogen pressure is mainly to suppress the decomposition of silicon nitride.**

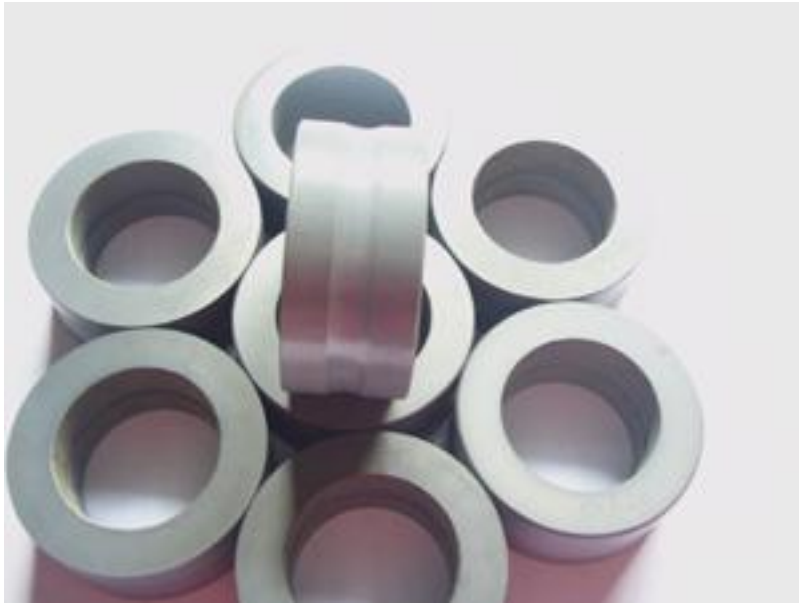
Manufacturing Methods of Silicon Nitride Ceramics

- **Hot-Isotropic-Pressure Sintering**
- **Put the powder or pre-load green body into the sheath (metal or glass)**
- **The high pressure gas is introduced into the furnace (100 ~ 200Mpa)**
- **At high temperatures, glass will melt into sticky matter or metal can have a good ability of plastic deformation to transmit pressure and make the products sintered densified.**
- **After cooling, remove the sheath and obtain sintered products.**
- **Hot-Isotropic-pressure-sintering can get fully densified silicon nitride ceramic, with less or no use of sintering aids, and the products are isotropic.**
- **Hot-Isotropic-pressure-sintering features expensive equipment, complex process (sheath required), and high production costs.**

Manufacturing Methods of Silicon Nitride Ceramics

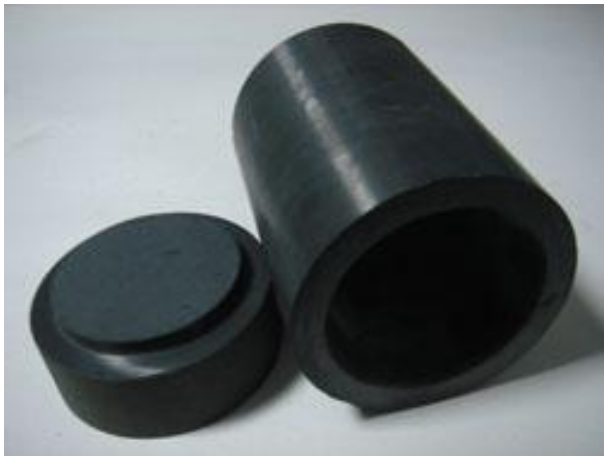
Other sintering methods (plasma sintering, microwave sintering, electric spark sintering, etc., not entering the production areas)

Applications of Silicon Nitride Ceramics



Silicon nitride ceramic guide pulley

Applications of Silicon Nitride Ceramics



Applications of Silicon Nitride Ceramics

- High hardness, wear resistance, resistance to corrosion from strong acids, no significantly decrease in the high temperature performance;
- Excellent thermal shock resistance, high oxidation resistance, operating temperature up to 1200 degrees;
- With self-lubricating properties, higher service life than conventional steel bearings.
- Delivery devices in high temperature equipment: When the high temperature reaches up to 1200 degrees, strength and hardness remain almost unchanged;
- High-speed operation areas: spindle bearings for high-speed motor, spindle bearings for machine tools, bearings for dental drills, bearings for computer hard drives, bearings for instrumentation;
- Aviation and aerospace fields: low linear expansion coefficient, stable and reliable in the environment of temperature changes, high vacuum fields, strong magnetic environments.

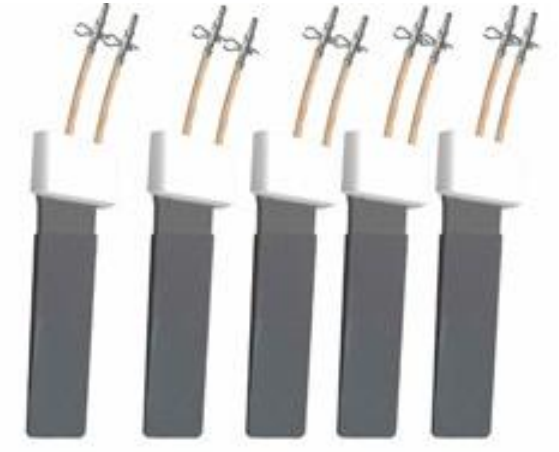
Applications of Silicon Nitride Ceramics

Silicon nitride ceramic glow plug

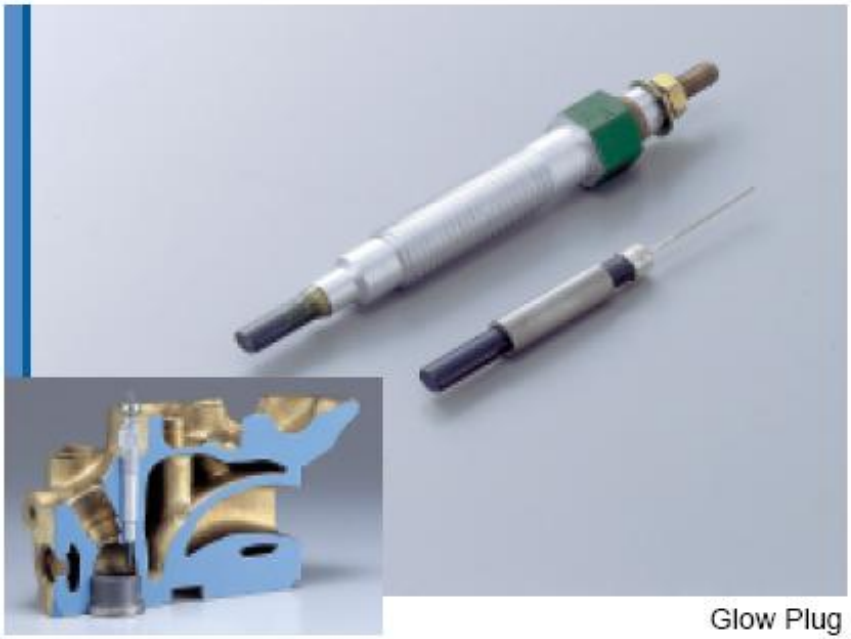
Applications of Silicon Nitride Ceramics

Applications of Silicon Nitride Ceramics

Applications of Silicon Nitride Ceramics



Automotive Related Heater Applications

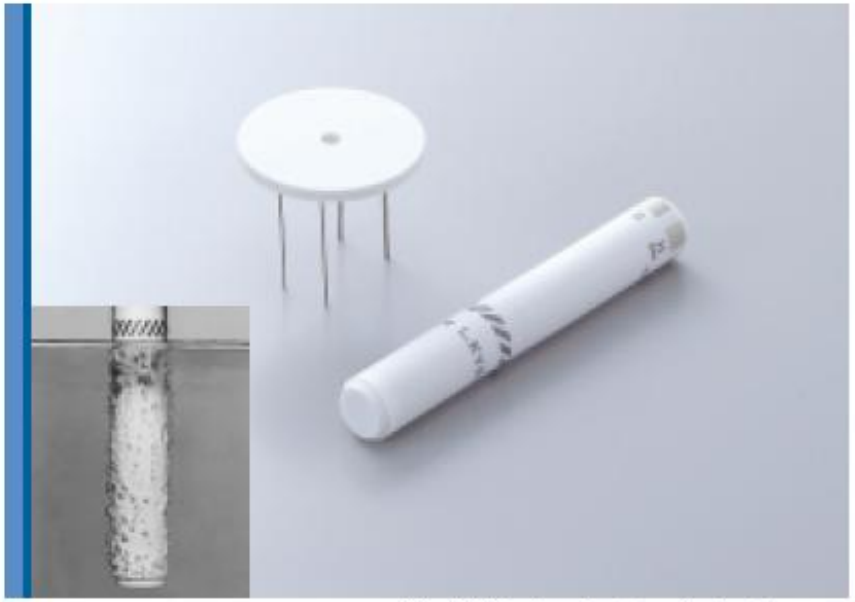


Glow Plug

Water-Heating Applications

Hot Water Heater

Intake (Burner) Heater



Liquid Heater for Small Appliances

Applications of Silicon Nitride Ceramics

Others

Heater for Toilet Water

Applications of Silicon Nitride Ceramics

Molten metal processing parts

Superior in thermal shock resistance and high temperature

strength, silicon nitride is less susceptible to corrosion from

molten metal, and is used for thermocouple protection

sheaths, molten aluminum jigs and molten metal pumps.

Manufacture of Silicon Nitride powder

www.visit-silicon.com