Breaking the N-SiC Barriers

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A new type of nitride-bonded SiC kiln furniture is giving ceramic manufacturers an even broader range of high-performance, low-mass kiln furniture options.

Typical structures in modern, low-mass kiln furniture systems include hollow shapes, such as posts and beams, and flat shapes, such as setter plates. Historically, alumina-, mullite- and cordierite-based refractories were chosen for kiln furniture due to their resistance to chemical and physical degradation at high temperatures. However, with the increasing trend toward higher throughput, efficiency and automation, many manufacturers and kiln builders have begun choosing high-performance materials based on silicon carbide (SiC).

These materials offer greater strength and stiffness than their oxide counterparts, which means that less mass is required to support the same load. SiC-based materials

Beams made with the new N-SiC material support a car structure in a roof tile tunnel kiln.

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also have high thermal conductivity, which, when combined with their lower mass, results in faster heating and reduced energy requirements. Finally, while oxide-based furniture tends to creep and warp, the SiC-based systems generally remain more rigid over a long period of high-temperature use. This is especially important in automated processes, which demand high tolerances for dimension, creep and warpage to ensure smooth operation. The higher durability of SiC kiln furniture also gives it greater longevity, enabling it to provide dramatic cost savings despite the increased initial investment required.

Recently, a new type of nitride-bonded SiC kiln furniture was developed that provides better oxidation resistance over a wide temperature range, increased coating life and fewer problems with sticking. With this new class of SiC kiln furniture, today's ceramic manufacturers have an even broader range of low-mass kiln furniture options.

Conventional Classes of SiC Furniture

High-performance SiC-based kiln furniture falls into four main classes: recrystallized SiC (R-SiC), sintered SiC (S-SiC), siliconized SiC (Si-SiC) and nitride-bonded SiC (N-SiC).

Recrystallized SiC kiln furniture is a pure SiC product with a maximum use temperature of 1650°C.[1] It is used in a broad range of applications in the form of posts, beams, rolls and flat shapes. However, due to its internal porosity, R-SiC can oxidize over long periods at elevated temperatures in oxidizing conditions.

Sintered SiC is the highest-strength SiC kiln furniture material on the market and resists oxidation up to temperatures of 1650°C.[2] It is typically offered in the form of beams and rolls. Its main disadvantage is its high initial cost.

Siliconized SiC is a dense, oxidation-resistant SiC product, in which the pores are filled with silicon.[3] Its use is restricted to service temperatures below 1350°C because silicon melts at ~1400°C. Exceptionally strong and stiff, Si-SiC is valued for its load-bearing capacity, particularly in the form of beams and posts.

Nitride-bonded SiC kiln furniture is strong and fine-grained, and is typically supplied as flat shapes (setter plates), beams, posts and other shapes.[4] It is used in a wide range of applications between 1200 and 1550°C. Despite its fine microstructure, N-SiC resists oxidation because it is protected by a dense, passivating glassy layer. However, the material is limited to higher-temperature applications because the glassy layer breaks down at lower service temperatures (e.g., 800-1100°C).

Figure 1 shows the strengths of each of these high-performance materials as a function of temperature.

Low-Temperature Challenges

In some ceramic processes, such as firing roof tile, the kiln furniture materials must be resistant to temperatures from 900-1150°C. Cordierite was typically the choice material for these applications, but it has a limited service life due to creeping and chipping, as well as an inefficient, high refractory-to-product mass ratio.

New designs with the low-mass, high-strength benefits of SiC-based kiln furniture require less energy and can be cycled faster than oxide systems. N-SiC would be an attractive material for this application, but it is not appropriate for extended use at low service temperatures. Consequently, most roof tile manufacturers employ a combination of Si-SiC beams and oxide setter shapes.

The glassy passivating surface layer of N-SiC impedes the penetration of oxygen from the atmosphere to minimize the reaction with the SiC/Si_3N_4 in the bulk of the material. However, when the material is used solely at lower temperatures (<1200°C), the silica layer is susceptible to damage, which leads to rapid oxidation and failure of the piece. The silica layer breaks down as a result of: 1) mechanical/handling damage, 2) cristobalite formation, and 3) bubbling of the silica layer.

Although handling damage is not frequently observed, it is a known cause of oxidation failure of N-SiC pieces. Manufacturers should ensure that parts are handled carefully. If damage occurs, the piece should be checked frequently to monitor degradation. For most high-service-temperature applications (>1200°C), the protective glass layer typically "heals"

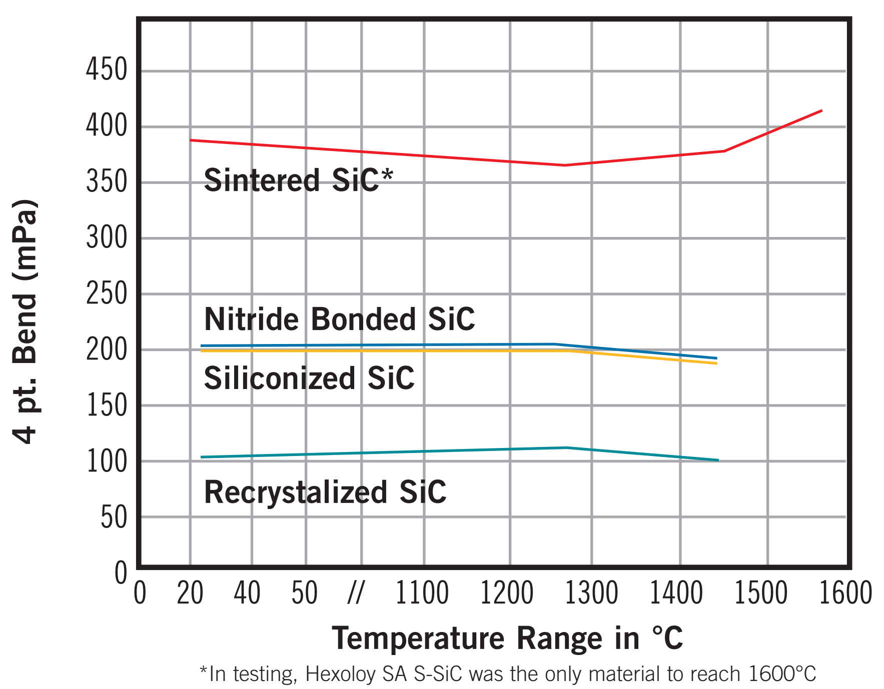

Figure 1. Strength of various high-performance materials as a function of temperature. (Note: Tests were performed only on products supplied by Saint-Gobain Industrial Ceramics.)

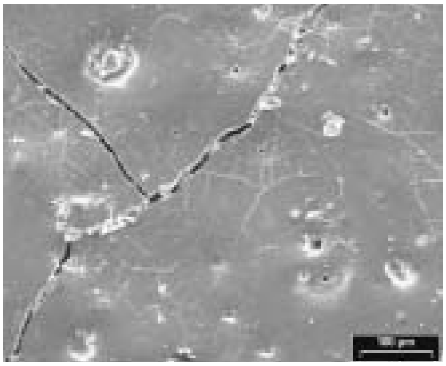

Figure 2. Cracks present in the glassy surface of a conventional N-SiC material after cycling in service conditions of ~900°C.

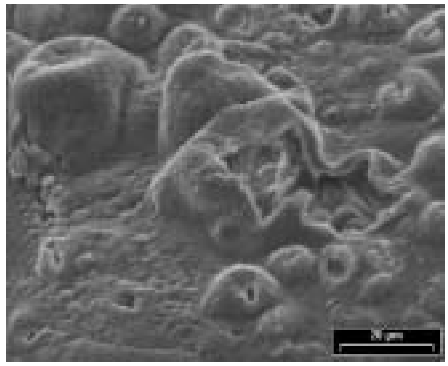

Figure 3. Conventional N-SiC oxidized at 900°C in steam for 500 hours shows damage to the surface glass from bubble formation.

itself, and the part will have a normal lifespan. Below 1200°C, the glass has less of a tendency to heal and might fail early.

Cristobalite can form in the high-silica-content glassy layer and, with thermal cycling, can initiate and propagate cracks. This can make the silica layer ineffective at protecting the bulk of the kiln furniture from oxidation (see Figure 2).

In a similar way, oxidation of the bulk can occur when the glass layer breaks down due to the formation of bubbles in the glass (see Figure 3). When the bubbles grow and burst, the openings left behind allow air to penetrate the microstructure and rapidly oxidize the part. Research has shown that bubbles are typically found in service conditions with high humidity. This is due to the following reaction sequence:

$$SiC + 2H_2O \rightarrow SiO_2 + C + 2H_2$$
$$2C + O_2 \rightarrow 2CO$$

This reaction sequence produces more gas than is taken in during the reaction. Due to the low solubility of CO in the glass, bubbles can form, grow and ultimately burst. Above 1200°C, the bubbles are smaller, and the gas is released quickly. At lower temperatures, the higher glass viscosity results in larger bubbles, which collapse and leave the bulk material unprotected.

In each case of silica layer breakdown, the damage normally re-heals under oxidizing conditions above 1200°C. However, at lower application temperatures, the passivating layer cannot re-heal due to the high glass viscosity and slow oxidation kinetics. As a result, bulk oxidation is allowed to continue locally. Over a short period of time, the internal oxidation can lead to cracks and warpage, which further accelerate the part's failure.

A New N-SiC Material

Research in low-temperature oxidation resistance has resulted in the development of a new class of N-SiC material that can be used at low service temperatures for extended periods. Unlike other N-SiC materials, the oxide layer remains protective at low service temperatures, thereby limiting oxidation and extending service life.

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One type of kiln furniture made with this material performs well over a wide range of service conditions.[5] It is comparable in strength and stiffness to other N-SiC materials, but it can withstand low-temperature degradation of the passivating layer due to its unique nature. The new material also enhances the life of applied coatings (compared to conventional N-SiC) and reduces sticking at elevated temperatures (up to 1550°C).

Another type of kiln furniture made with the new N-SiC material exhibits the best results in low temperature oxidation.[6] Targeted for low-temperature (<1200°C) service conditions only, it enables the use of N-SiC products over the entire 800-1550°C temperature range.

Application Opportunities

The low-temperature oxidation resistance, increased stability, increased coating life and reduced sticking capabilities of the new N-SiC kiln furniture enable it to be used in a variety of applications, including roof tile, porcelain and advanced ceramics manufacturing.

Roof Tile. The low-temperature oxidation resistance of the new N-SiC kiln furniture makes it ideal for use in roof tile kilns, where kiln furniture must be oxidation-resistant at low service temperatures, as well as resistant to bubbling resulting from the high humidity typical in the firing of clay-based roof tiles.

In one test, flat shapes of the new kiln furniture were cycled for more than 12 months in a European roof tile kiln without any sign of degradation or bulk oxidation. In a second trial, beams were cycled in a roof tile kiln for more than 11 months (as of June 2003) without any signs of damage.

Porcelain. One form of the new N-SiC kiln furniture is stable in both low- and high-temperature environments.[5] Due to a surface that is rougher than most fine N-SiC materials, it also offers advantages of increased coating life and reduced sticking, particularly in applications where elevated temperatures normally cause a buildup of glass.

At a porcelain manufacturing site with an application temperature of ~1400°C, the coating life on setters made with the new N-SiC material was improved by about 30% compared to similarly coated conventional N-SiC setters. Product performance was also comparable to conventional N-SiC when used for extended periods.

Advanced Ceramics. The combined high- and low-temperature oxidation resistance of the new N-SiC material makes it especially attractive for use as posts in applications with a range of temperatures—such as when one end is cemented into an insulated base while the other end experiences the normal firing temperatures of the kiln.

This type of application would normally pose a problem for high-service-temperature kilns (e.g., >1350°C) where Si-SiC kiln furniture cannot be used, and where conventional N-SiC furniture can suffer from oxidation damage near the insulated bottom of the post. The new N-SiC material operates well in both environments, making it an ideal choice for this application. Tests of posts made with the new N-SiC material have been in progress for more than 12 months (as of June 2003) with good performance to date.

New Kiln Furniture Options

As ceramic manufacturers continue to look for ways to increase production efficiencies, automate operations and reduce energy consumption, kiln furniture is an obvious place to start. SiC systems offer greater strength and stiffness than conventional oxide kiln furniture, with less mass required to support the same load. They also offer faster heating, reduced energy requirements, higher durability and greater longevity.

With the recent development of a new N-SiC kiln furniture material, companies can enjoy the benefits of higher-performing, low-mass SiC kiln furniture in almost any firing application. ⊕

For more information about high-performance, low-mass SiC kiln furniture, contact Saint-Gobain Industrial Ceramics, M.S. 506-301, 1 New Bond St., P.O. Box 15136, Worcester, MA 01615-0136; (508) 795-5577; fax (508) 795-5011; e-mail ceramicsystems@saint-gobain.com; or visit www.refractories.saint-gobain.com.

References

1. Crystar®, a registered trademark of Saint-Gobain Industrial Ceramics, is an example of R-SiC.
2. Hexoloy® SA, a registered trademark of Saint-Gobain Industrial Ceramics, is an example of S-SiC.
3. Silit® SK, a registered trademark of Saint-Gobain Industrial Ceramics, is an example of Si-SiC.
4. Advancer®, a registered trademark of Saint-Gobain Industrial Ceramics, is an example of high-temperature N-SiC.
5. Annasicon® RTH (patent pending), developed and supplied by Saint-Gobain Industrial Ceramics.
6. Annasicon® RT (patent pending), developed and supplied by Saint-Gobain Industrial Ceramics.