Ceramic Fiber and the Development of Insulating Technology

1. Introduction

The ceramic fiber business of Shinnikka Thermal Ceramics Corporation began in March 1984 when its Sakai Works (then Nippon Steel Chemical Sakai Works) started production of ceramic fibers after several years of preparatory arrangements. The continuous reheating furnace having all-ceramic fiber lining, high thermal efficiency and low thermal inertia that was adopted for the plate mill (put into operation July 1986) of Kimitsu Works of Nippon Steel led to the birth of Shinnikka Thermal Ceramics, and the subsequent expanded use of Shinnikka's thermal ceramics in steelmaking processes is a real milestone in the growth of the company.

In November 2007, Shinnikka Thermal Ceramics launched full-scale production of its environment-friendly product "Bio-Soluble Fiber" (trade name: Superwool). Since then, the company has been pressing ahead with the development of markets for the product.

This paper outlines the development of ceramic fiber-based heat insulating technology for the steel industry. It also discusses the possibility of expanding the use of Superwool in the steel industry.

2. Types and Characteristics of Ceramic Fiber

2.1 Characteristics of ceramic fiber

Ceramic fiber (CF) is a man-made mineral fiber consisting mainly of alumina and silica. Because of its exceptionally low thermal conductivity, CF dissipates little heat from the furnace and has remarkable energy-saving properties (**Fig. 1** (a)). In addition, because of its low density and low thermal inertia, CF facilitates controlling the temperature inside the reheating furnace (Fig. 1 (b)). For those reasons, the CF module (Z-BLOK) has been increasingly used for the inner linings of various reheating furnaces at steelmaking plants, etc.

2.2 Types of ceramic fiber and manufacturing processes

Ceramic fibers are largely divided into vitreous alumina-silica ceramic fiber (vitreous CF) whose service temperature is below 1,250 ℃ and crystalline alumina ceramic fiber (crystalline CF) whose service temperature is above 1,250℃.

(1) Vitreous CF manufacturing process (see **Fig. 2**)

Vitreous CF is manufactured by the melting and fiber-making process. A mixture of raw materials—mainly alumina and silica—is melted at about 2,000℃. At Shinnikka Thermal Ceramics, the molten mixture is ejected through a nozzle onto rotors turning at high speed and made into a bulk (raw fibers) by the centrifugal force of the rotors (spinning method). There is another fiber-making method in which the mixture of raw materials is blown by compressed air or steam (blowing method). A stack of bulks is lubricated and subjected to needling. The lubricant is then removed by heating to create a blanket.

The maximum service temperature of vitreous CF differs according to its constituent raw materials. For example, there is a 1,260℃ grade made from high-purity alumina and silica or kaolin clay, and a 1,400℃ grade that is made from high-purity alumina, silica and zirconia.

(2) Crystalline CF manufacturing process

Since the molten raw material for crystalline CF contains a large proportion of alumina and has low viscosity, the melting & fiber-making process that is applied to vitreous CF cannot be used to manufacture crystalline CF. Therefore, a precursor fiber-making process is used to manufacture crystalline CF. In this process, a fiber precursor solution containing aluminum is spun at room temperature into precursor fibers, which are crystallized by baking at temperatures of 1,000℃ or higher and made into a bulk. A blanket is manufactured

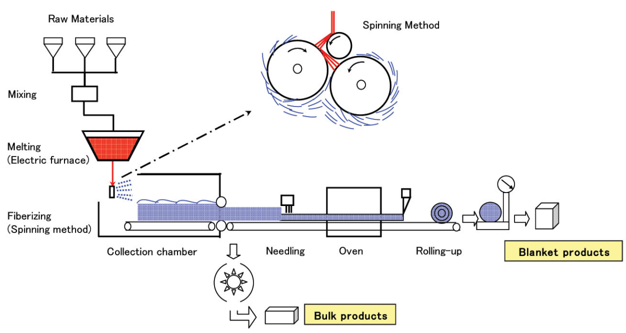

Fig. 2 Manufacturing process for vitreous ceramic fiber products

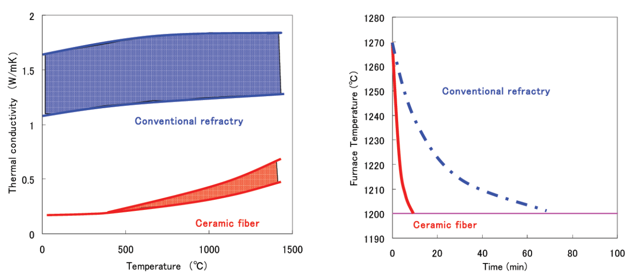

Fig. 1 Comparison of ceramic fiber and conventional refractory

Fig. 3 Main ceramic fiber products

by subjecting precursor fibers to needling before they are baked.

(3) Ceramic fiber products (see **Fig. 3**)

The bulks and blankets mentioned above are processed into various types of fiber products. Z-BLOK, which is widely used as a lining material for steelmaking equipment, is a module made by folding a blanket in the form of bellows and fitting metal supports to it. There are many other ceramic fiber products, such as sheets, boards, die-formed products that are specially shaped using a wet process, and ropes, tapes, and cloths, etc. by applying spinning technology.

3. Development of Heat Insulating Technology for the Steel Industry

3.1 Main uses

Table 1 shows the main uses of CF linings in the steel industry. Since the CF lining is a light structure made of fibers, it is not very strong and is highly reactive with external materials. Therefore, it is unsuitable for applications in which it comes into direct contact with molten metal or steel products. It is used mainly for heat-insulating covers, reheating furnaces and heat-treatment furnaces. The CF lining is also used as blanket/paper for the sealing material around the tundish, vacuum-formed shapes (VFS) as backup for various types of refractory, and textile items for packing the coke oven, etc.

As already mentioned, a continuous reheating furnace with all-ceramic fiber (CF) lining, high thermal efficiency and low thermal inertia was first installed at the plate mill (operational from July 1986) at Kimitsu Works of Nippon Steel.[1, 2] Since then, the application of CF linings in the steel industry, including other steelworks at Nippon Steel, has been expanded.

In retrospect, it is clear that (1) the reinforcement of heat insulation and the reduction of thermal inertia made possible by the application of CF modules to the furnace ceiling and side walls, (2) the reduction of heat loss (caused by water cooling) by the application of CF modules to the skid support, and (3) the introduction of non-water cooled partition walls using CF modules, were all related to furnaces employing all-ceramic fiber linings.

In the above achievements, the invention and commercialization of crystalline CF played an important role. Conventional vitreous CF has two major drawbacks. One is that in the high-temperature region exceeding 1,000℃, it shrinks markedly with the progress of crystallization. The other is that it easily reacts with in-furnace substances (scale is a typical example) to produce other substances with low melting points. By contrast, crystalline CF does not shrink much even at high temperatures (up to approximately 1,500℃) and is free of embrittlement due to crystal transformation. Therefore, it remains resilient over a wide temperature range.

3.2 Major trends in CF heat-insulating technology

It may be said that the history of CF lining application technology is one of technological developments to replace conventional refractory linings of various structures and parts with CF linings to help realize new production processes aimed at refining steel quality, improve productivity and save energy. Since the commercialization of crystalline CF paved the way for the spread of CF linings in the steel industry, the main emphasis in the development of CF lining technology has been placed on (1) improving the quality of crystalline CF, and (2) developing a new lining structure using crystalline CF.

Table 2 shows the major trends for R&D into CF linings. It should be noted that in developing new uses and new application technologies, Shinnikka always works in close cooperation with the refractory engineering departments of the steelworks of Nippon Steel, Nippon Steel Engineering (former Nippon Steel Plant Division) and the Refractory Ceramics R&D Division of Nippon Steel.

3.2.1 Trends in crystalline CF technology development

The improvement in crystalline CF quality has been largely achieved in two stages (**Table 3**). In the first stage, non-fiber particles (“shots”), which incidentally occur in the fiber-making process, have been significantly reduced and the tensile strength of blankets has been markedly increased, although the increase in tensile strength differs according to the blanket thickness (Table 3, **Fig. 4**: MLS (low-shot blanket)). In the surface-treatment process, in order to prevent shots contained in CF from falling onto and damaging the steel sheet being treated, it was common practice to apply an SUS sheet or long-fiber cloth to the surface of the CF lining at the site. By employing Z-BLOK modules whose surface is previously covered with a low-shot crystalline CF, it has become possible to omit the burdensome work of applying SUS sheet, etc. at the site. In addition, the improvement in the tensile strength of blankets in the high-temperature region has made it possible to manufacture longer Z-BLOK modules for partition walls of reheating furnaces and improve the durability and reliability of Z-BLOK modules.

In the second stage, by properly controlling the crystal structure of crystalline CF, the strength of single fibers has increased remarkably while the tensile strength of the blankets has improved markedly (Table 3, Fig. 4: MLS-2 (high-strength, fine-crystal product)). Blankets with this crystal structure do not weaken even under high temperatures (up to 1,250℃) and are flexible. Therefore, their applica-

Table 1 Main applications of CF linings in steel processes

Process	Application	Aim	Material	Product
Steelmaking	Ladle cover	Hot insulation of molten metal	Crystalline CF	Z-BLOK
	Carrier car	Hot insulation of slab	Amorphous CF	Z-BLOK
Reheating furnace	Ceiling, wall	Furnace casing insuiation	Crystalline CF	Z-BLOK
	Skid support	Reduction of heat loss caused by water cooling	Crystalline CF	Z-BLOK Blanket VFS
	Partition wall	Reduction of heat loss caused by water cooling	Crystalline CF	Z-BLOK
Surface treating, heat-treating furnace	Ceiling, wall	Furnace casing insulation	Crystalline and amorphous CF	Z-BLOK
	Burner tile	Low thermal inertia	Crystalline CF	Z-BLOK VFS

Table 2 Major technology developments trend of CF linings

	Process	Application	Requirement	Technology development of crystalline CF		
				Conventional product	Thermal insulation improvement, reduction in the amount of falling shot and strength improvement of blanket due to shot content reduction	Strength improvement of single fiber due to crystallization control Strength improvement of blanket
Application technology (lining structure development)	Reheating furnace	Ceiling, wall	Dealing with configuration	A typical Z-BLOK		
			Durability enhancement -Scale resistance -Dealing with regenerative burner	Scale resistant surface coating materials		
			Repairing technology	Repairing materials for joint		
		Skid support	Durability enhancement Installability enhancement	VFS skid support		
		Partition wall	Durability enhancement Installability enhancement		Z-BLOK partition wall	
	Heat-treating furnace	Ceiling, wall	Prevention of scar formation on steel plate		Unwrapped Z-BLOK	Unwrapped Z-BLOK
		Burner tile	Low thermal inertia	Z-BLOK type burner tile		
			Durability enhancement -Wind velocity resistance	VFS burner tile		Z-BLOK type burner panel

Table 3 Transition in quality improvement of crystalline CF

Major quality item		Crystalline CF blanket		
		M ➡	MLS ➡	MLS-2
		Conventional product	Shot content reduction	Strength improvement of blanket
Chemical composition (%)	Al_2O_3	72		
	SiO_2	28		
Mineral composition (%)		Mullite		Mullite, δ alumina
Shot content ≧45 μm (%)		23	5	5
Single fiber tensile strength (MPa)		1,000		1,500
Linear shrinkage (%) 1,600℃×24h		1		

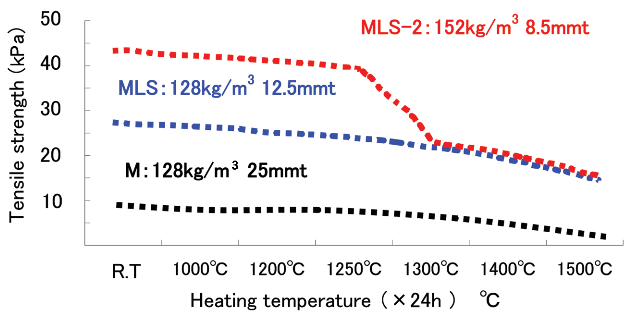

Fig. 4 Tensile strength of typical crystalline CF blanket

tion is being expanded to lining material for the parts around the burners of reheating furnaces where the influence of gas flow rates is not negligible.

3.2.2 Trends in CF lining application technology

(1) CF lining for reheating furnaces

(i) Crystalline CF Z-BLOK

As mentioned above, the crystalline CF does not shrink much even at high temperatures and maintains its compressive resilience over a wide temperature range. Therefore, it is suitable for use as a lining for reheating furnaces. However, since it is costlier than the vitreous CF, a combination type Z-BLOK that employs crystalline CF only in those parts which are exposed to high temperatures is used more often than not (BH Type and B Type in **Fig. 5**).

Depending on the shape of the reheating furnace, standard box-shaped modules alone are insufficient. Therefore, various types of deformed modules, such as the corner type, lintel type and double type, are used for the appropriate parts.

(ii) Non-water cooled partition wall

The 1.4-m long non-water cooled Z-BLOK partition wall was

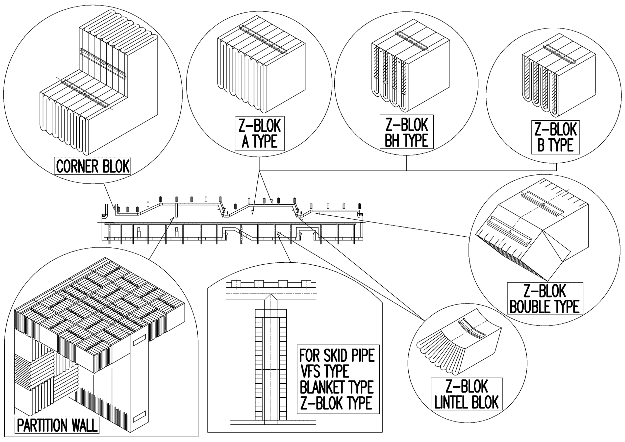

Fig. 5 Typical CF linings in reheating furnace

adopted for the first time for a reheating furnace (operational from May 1995) by T Company. Up until now, the partition wall has been in use without any particular problems. However, a partition wall of the same specifications (length: 2.0 m) adopted for a large-sized reheating furnace (operational from January 2001) at Nippon Steel's Sakai Works broke halfway and collapsed in less than a year. That phenomenon reflected not only the use of longer partition walls, but also the different furnace operating conditions and in-furnace atmosphere caused by the introduction of a regenerative combustion system (regenerative burners) as a promising means of saving energy and controlling environmental pollution.

The damage to CF linings became conspicuous as the hotter, wider and longer flames made direct contact with the CF linings and the scale fanned by the strong flames violently corroded the CF linings. Eventually, the blanket used as the base material for the CF lining was replaced with MLS which is capable of much greater tensile strength even at high temperatures and a coating material with excellent resistance to scale and thermal shrinkage even under the high temperatures applied to the CF lining surface that comes into direct contact with the flames (**Fig. 6**). Now, non-water cooled Z-BLOK partition walls exceeding 2.0 m in length are used in the large-sized reheating furnace at Sakai Works mentioned above, the hot rolling/reheating furnace at Yawata Works, the NCR reheating furnace at

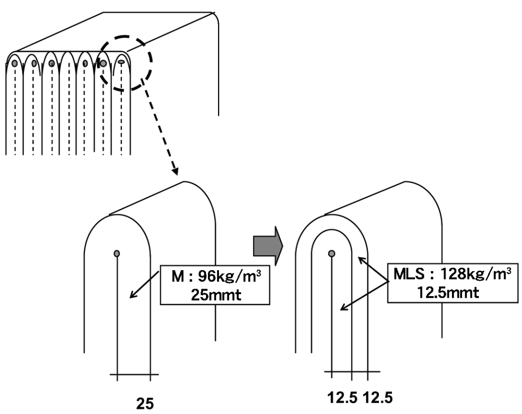

Fig. 6 Standard Z-BLOK type partition wall

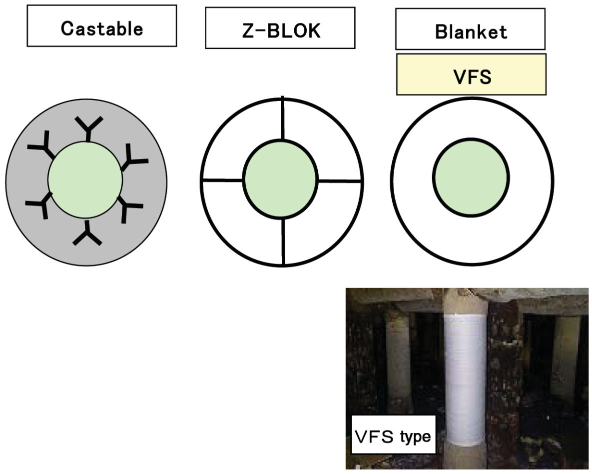

Fig. 7 Cross-section profile of typical skid support insulation and photograph of VFS type insulation

Muroran Works, and the large-sized reheating furnace at Kimitsu Works, etc. The risk of an unexpected accident occurring with them has been reduced.

(iii) Skid support (see **Fig. 7**)

From the standpoint of reducing the loss of heat caused by the cooling water, an attempt has been made to apply fibrous heat-insulating materials with low thermal conductivity for the skid supports. However, since materials which have both low thermal conductivity and high durability are hard to find, each individual steelworks employs heat-insulating structures of different specifications for their reheating furnaces on a trial-and-error basis. Among them, the method in which a doughnut-shaped blanket provided with cuts in it is fitted to the skid support proved advantageous in terms of thermal conductivity and applicability. However, it was disadvantageous in terms of durability.

As a means of improving the durability while maintaining the advantages of the above method, we adopted as the base material a hard vacuum-formed shape (VFS) that offers thermal conductivity comparable to that of the blanket.[3] In addition, we devised a new fitting method, in which the skid support is enclosed by a couple of semicircular parts in the form of a doughnut. The applicability of this new method is the same as that of the former method. The hard fibrous base material has improved both the resistance to scale and thermal shrinkage and adhesion of the coating material. It was found that the durability of the skid support heat insulation in the hot rolling reheating furnace at Nagoya Works is about 2.5 times better than the conventional blanket heat insulation.

(2) CF lining for heat-treatment furnace

(i) Crystalline CF Z-BLOK

For heat-treatment furnaces, various types of lining structures for heat insulation are employed according to the purpose and temperature of the heat treatment. In the temperature range up to 1,000 ℃, a lining structure made of inexpensive vitreous CF is generally adopted. In order to prevent shots contained in the CF from falling onto and damaging the steel being treated, it is common practice to apply an SUS sheet or long-fiber cloth to the CF lining surface at the site. However, the development of a low-shot crystalline CF blanket has made it possible to omit the burdensome work of applying an

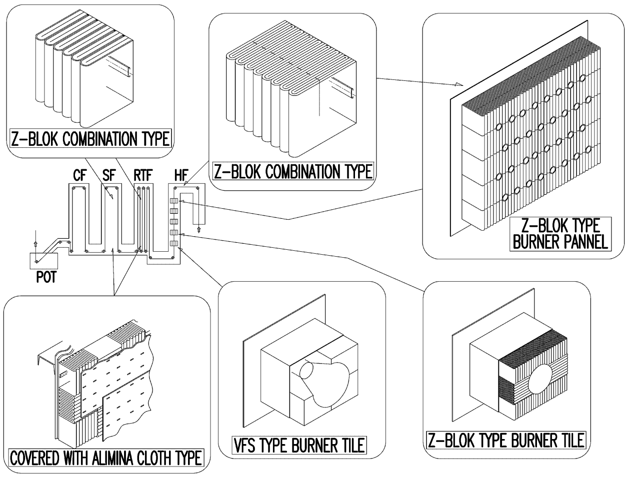

Fig. 8 Typical CF linings in heat-treating furnace

SUS sheet, etc. by using a Z-BLOK module covered with the low-shot crystalline CF blanket only on the surface (**Fig. 8**).

(ii) Burner panel

In the hearth furnace (HF) of the No. 4 continuous galvanizing line at Kimitsu Works that was modified in December 2005, the linings of the shell and burner panels were all made of monolithic refractory because the steel sheet was heated by jetting high-speed combustion gas from the reducing burners onto it. During the modification, the monolithic refractory linings were replaced with CF linings (a ceramic sleeve was employed for the burner combustion tube). Z-BLOK modules covered with MLS-2 blanket on the surface were used for the CF linings.

The MLS-2 blanket has proved to have excellent resistance to air velocity and a measure of scale resistance.

(iii) Burner tile

In the non-oxidizing furnaces (NOFs) for Nos. 3 and 4 continuous galvanizing lines (CGL) at Nagoya Works, the ceilings and walls had already been provided with Z-BLOK linings. However, since there was some concern that the monolithic refractory burner tiles may be damaged by thermal shock, it was necessary to raise and lower the furnace temperature slowly. Even so, the burner tiles were damaged from time to time.

At present, in view of the burner capacity, a Z-BLOK burner tile is used for the No. 3 CGL and a VFS burner tile is used for the No. 4 CGL. Both tiles are given special fiber orientation from the standpoint of securing sufficient resistance to air velocity.

4. Bio-Soluble Fiber "Superwool" [4)]

4.1 Classification of man-made vitreous fibers based on carcinogenicity

The news in recent years about the health risks associated with asbestos must be fresh in everyone's mind. To date, no human health risks, such as the development of tumors, caused by ceramic fiber has been reported. However, in 1997, the European Union (EU) added MMVFs (man-made vitreous fibers) to the "Classification of Carcinogenic Substances" based on the EU Directive 67/548/EEC.

Since then, vitreous CF has been included in Category 2 (To be

Table 4 Examples of carcinogen classification

European Union (EU)	IARC (WHO)
Category 1 Known to be a human carcinogen Asbestos	Group 1 Carcinogenic to man Asbestos
Category 2 Carcinogenic to animals. To be used as if it is carcinogen to man. Refractory ceramic fiber Micro glass wool	Group 2A Probable human carcinogen Ultraviolet radiation
Category 3 There is some doubt but information is not sufficient to classify in category 2. Glass wool Rock wool	Group 2B Possible human carcinogen Refractory ceramic fibers Special-purpose fiber
Category 0 Substances or preparation which have been received but not classified. Continuous glass filament Superwool	Group 3 or 4 Not classifiable Glass wool Rock wool

used as if carcinogenic to man) as per EU Directive 97/69/EC, etc. Accordingly, the methods of packing and marking are specified. **Table 4** shows the EU classification, together with the classification by the International Agency for Research on Cancer (IARC), an external affiliate of the World Health Organization (WHO). The EU countries are tightening their regulations on the use of vitreous CF, including the standards for concentrations of exposed fibers at workplaces. In Germany, the use of vitreous CF in the construction industry is prohibited.

Animal experiments based on the above EU Directive have demonstrated that the directive does not apply to the bio-soluble fiber "Superwool." This man-made vitreous fiber is classified under Category 0.

4.2 Types and characteristics of Superwool

The typical chemical composition of Superwool is shown in **Table 5**. Superwool consists mainly of SiO_2, CaO and MgO, whereas vitreous CF consists mainly of Al_2O_3 and SiO_2. Although the mechanism of bio-solubility has not been completely clarified, a few compositions that met the required bio-solubility, heat resistance and productivity were selected from among a huge number of candidates.

Superwool's linear shrinkage on heating—one of the indexes of heat resistance—is shown in **Fig. 9**, and its working temperature range

Table 5 Superwool types and chemical compositions

Chemical composition		SC 1260	Superwool	
			607	607HT
SiO_2	(%)	52-56	62-68	70-80
Al_2O_3	(%)	44-48		
CaO+MgO	(%)		25-40	18-25
Others	(%)	< 3	< 1	< 3

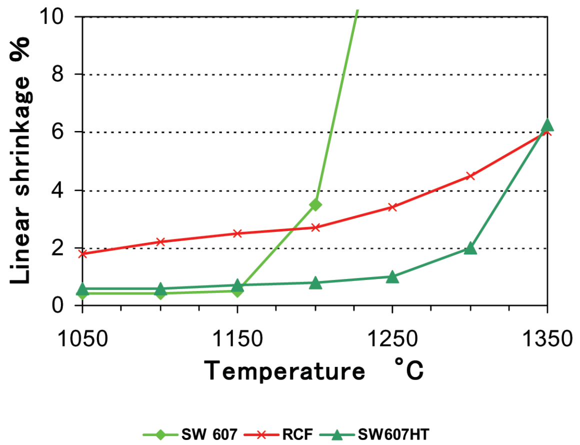

Fig. 9 Linear shrinkage after heat treatment at each temperature for 24 hours

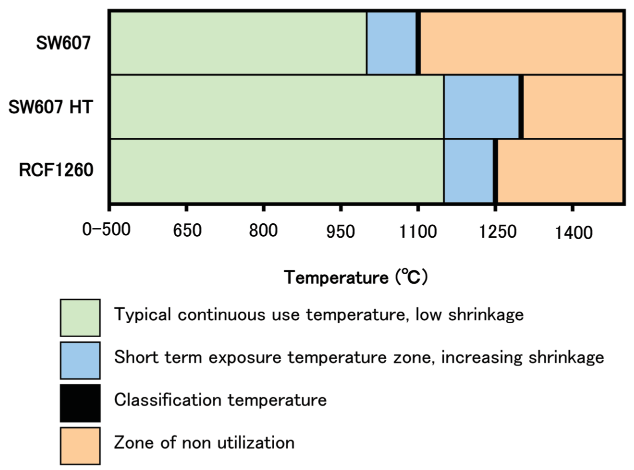

Fig. 10 Superwool type and classification temperature

is shown in **Fig. 10**. The linear shrinkage of SW607, a general-purpose grade, is less than that of the 1,260℃ grade of vitreous CF in the temperature range up to around 1,100℃. However, since the linear shrinkage of SW607 begins to increase sharply at 1,150℃, the classified temperature is set at 1,100℃. In the case of SW607 HT, a high-temperature grade that was developed recently, the linear shrinkage is about 2% even when heated to 1,300℃. Thus, SW607 HT is positioned as an alternative to the 1,260℃ grade of vitreous CF.

In terms of the linear shrinkage on heating, Superwool is comparable to vitreous CF. It should be noted, however, that with respect to the heat-resisting performance required in a particular use, Superwool is not comparable to vitreous CF yet because of its characteristics related to bio-soluble functions. For example, Superwool easily reacts with other materials to produce substances with low melting points and is susceptible to abnormal shrinkage. Besides, since the crystallization temperature during reheating is low, embrittlement of the crystallized fiber imposes certain limits on the use of Superwool.

4.3 Development of uses for Superwool

The Sakai Works of Shinnikka Thermal Ceramics started full-scale production of SW607 in November 2007. At that time, the company implemented equipment modification and introduced a new operational management system appropriate to the "low-shot technology" it had newly developed. As a result, it has become possible for the company to supply SW607 that is more heat resistant and stronger than the former SW607 product (trade name of the new product: Superwool 607 plus). At present, the company is developing new uses for Superwool in Japan and pressing ahead with the replacement of vitreous CF by Superwool.

(1) Main uses

In the EU, which has some of the world's highest safety-conscious standards, sales of Superwool have been more than double those of vitreous CF since 2003. In the EU, the main uses for Superwool in civilian requirements are "heat insulation of kitchen utensils for home and business use" and "fire protection for marine vessels and buildings." Concerning industrial applications, such as "heat insulation of exhaust gas boilers (HRSG) at gas turbine combined-cycle power plants" and "reinforcement of brake pads," Superwool has been increasingly used in place of vitreous CF. In Japan too, Superwool is mainly used for the purposes mentioned above.

(2) Uses in steelmaking processes

In Japan, the refractory departments of steelworks, etc. are testing and evaluating the applicability of the general-purpose grade SW607 in their steelmaking processes.

At Kimitsu Works, the vitreous CF Z-BLOK linings of its bell-type batch annealing furnaces have been gradually replaced with SW607 Z-BLOK linings since 2005.

In the EU, the use of the high-temperature grade SW607 HT that was developed recently is increasing. In those reheating furnaces that are operated in the temperature range 1,000℃ to 1,100℃, SW607 HT Z-BLOK is used as a lining material. The use of SW607 HT as a consumable material for "heat insulation of ladle gate slides" and "heat insulation of tundishes" has also been reported. It is expected that SW607 HT will be tested and evaluated in Japan in the future.

5. Conclusion

Shinnikka Thermal Ceramics recognizes the importance of its efforts to develop heat-insulation technology for the steel industry as part of the technology to save energy in the bid to curb global warming. The company has several problems that remain to be resolved. On the other hand, improving the efficiency of steelmaking processes is concomitant with the more stringent conditions for heat-insulating materials. This implies that there is no end to the improvement in qualities of heat-insulating materials. In addition, proposing new environment-friendly products has become indispensable in view of the aggravating environmental problems.

The company has begun to develop bio-soluble fibers of a higher temperature grade. After all, it is necessary for us to develop new heat-insulating materials to help conserve energy and protect the environment in close cooperation with everyone concerned.

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