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High Temperature Low Bio-persistent Wool Development

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Abstract

High temperature insulation wool, which is a fire-resistant with heat insulation material, has been applied in the field of steel processing as an energy-saving material that contributes to the prevention of global warming. At present, high temperature insulation wool with low bio-persistent fiber with consideration for safety has been developed. This paper outlines the development of heat insulation technology for steel processing, introduces low bio-persistent fibers, and expands the application of Superwool® XTRA, in the steel process.

1. Introduction

The high temperature insulation wool business of Shin-Nippon Thermal Ceramics Corporation started in 1984 when the company began producing refractory ceramic fiber (RCF) (product names: SC1260 and SC1400) at the Sakai Plant (former Nippon Steel Chemical Co., Ltd. Sakai Works). RCF is an amorphous and man-made vitreous fiber (MMVF). After that in 1986, the Plate Plant of the Kimitsu Works adopted module products (product name: Z-BLOK) that used poly crystalline wool (PCW) (product name: SC1600), which is a crystalline fiber. Since then, applications of high temperature insulation wool to products used in the steel process have been continued up to the present day.

After that, Europe and the United States started discussing whether RCF, which is a type of high temperature insulation wool, was safe for human health. Shin-Nippon Thermal Ceramics gradually started selling alkaline earth silicate wool (AES) (product names: Superwool® Plus and HT), which was an amorphous ceramic fiber with low bio-persistence (or bio-soluble) and can replace RCF.

However, AES could not replace high-temperature RCF. As the latest product, we developed a high-temperature low bio-persistent fiber that met the Japanese regulations on RCF enforced in 2015 to replace RCF and put Superwool® XTRA (former name: Superwool® XT) on the market in 2019. Superwool® XTRA is a low bio-persistent fiber with the same heat resistance as 1400-grade RCF for high temperatures. The development of Superwool® XTRA completed the development of low bio-persistent fiber types that can replace all the grades of RCF.

This paper introduces high temperature insulation wool first and then describes the safety of such wool to human health, along with an outline of the development of heat insulation technologies for steelmaking. This paper also introduces Superwool® XTRA that was most recently developed as a low bio-persistent fiber and its possible applications in the steel industry.

2. Characteristics and Types of High Temperature Insulation Wool

2.1 Characteristics of high temperature insulation wool

MMVF is made by combining minerals, ore, slag, rocks, inorganic oxide powder, and other raw materials in various combinations and melting the combined materials to make fibers. MMVF is widely used as fire-resistant materials and heat-insulating materials.[1] In this paper, among MMVF, RCF, AES, and PCW are defined as high temperature insulation wool. As characteristics of the high temperature insulation wool, they can be used at higher temperatures compared to other types of MMVF. Therefore, they have been widely applied in the steel process where operations at high temperatures are required. In addition, among all types of refractories, the thermal conductivity of RCF, AES, and PCW is very low, their energy-saving effects are high, and their density and heat capacity are also low. Therefore, the temperature adjustment is easy when the temperature at the furnace bodies is changed. By drawing on these properties, they have been used as fiber linings for heating furnaces and heat treatment furnaces.

2.2 Characteristics of RCF

RCF is an alumina-silica amorphous fiber that is used at the maximum service temperature of 1 400°C or lower. This paper describes the basic properties of RCF using SC1260 and SC1400 as indicators. Various companies sell materials with almost the same quality according to JIS R 3311 and other standards. **Table 1** lists the chemical composition of RCF. The maximum service temperature has been determined for each grade: That of SC1260 is 1 260°C and its chemical composition is Al_2O_3-SiO_2. SC1400 with higher heatproof temperature was developed by adding zirconia (Al_2O_3-

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Table 1 Chemical composition of RCF

	Classification temperature (°C)	Al_2O_3 (wt%)	SiO_2	ZrO_2
SC 1260	1 260	46	54	–
SC 1400	1 400	35	50	15

Table 2 Chemical composition of AES

	Classification temperature (°C)	Al_2O_3 (wt%)	SiO_2	CaO+MgO
Plus	1 200	–	65	35
HT	1 300	1	74	25

SiO_2-ZrO_2) and its maximum service temperature is 1 400°C.

RCF has been widely used as fire-resistant materials for industrial furnaces, in particular, as a substitute for asbestos thanks to its high temperature properties. However, RCF has some problems: In the temperature range over 1 000°C, the progress of crystallization gradually causes heat shrinking and as the temperature increases, the larger the shrinkage rate is; and RCF tends to turn to substances with low melting points as a result of the reaction with some components in furnaces (typically, scales). Therefore, if RCF is used for an extended period of time, it is recommended that it be used in temperature ranges lower than the maximum service temperature.

2.3 Characteristics of AES fiber

There are no JIS and other standard specifications for AES fiber in Japan and various companies have developed various types of AES fiber. This paper describes the basic properties of AES fiber with Superwool® Plus and Superwool® HT as indicators. **Table 2** lists the chemical composition of AES. The product names have been determined for each classification temperature (the shrinkage rate should be smaller than 4% when the product is heated at the applicable temperature for 24 hours). The classification temperature of standard type Superwool® Plus is 1 200°C and that of high-temperature type Superwool® HT is 1 300°C. The main component of Superwool® Plus and Superwool® HT is SiO_2; and CaO and MgO are added as alkaline earth metals such that their total value would exceed 18% in consideration of safety to human health (SiO_2-CaO-MgO). **Table 3** shows the physical properties of AES.

The thermal conductivity of Superwool® Plus is lower than that of RCF products thanks to its low shot rate. Although applications to the steel process are limited due to the low classification temperatures, it is the most energy efficient at low temperatures. A typical application to materials other than those in the steel process is fire-resistant materials for ships. By making good use of the high fire resistance and low thermal conductivity, the fire resistance is maintained while the weight is reduced, which can reduce the weight of ships, contributing to the development of energy-efficient or higher-speed ships.

The shrinkage rate of Superwool® HT is in the same category as RCF1260. The product is mainly used as a substitute for RCF1260 in applications in the steel process.

Meanwhile, AES has some problems. One is that its crystallization temperature is lower than that of RCF. Compared to RCF, AES fiber becomes harder and weaker after heating and thereby its durability is poor. As a result, there is a concern that the surface may be thinner and may separate in the long-term use. Therefore, AES has been used only for part of heating furnaces at present. In addition, there is another concern regarding work environments. As shown in **Table 4**, it was found that the work environments worsen when AES is used at sites. It irritates the skin of workers, causes skin rashes, and produces more dust. Some researchers have reported that since the fiber diameter of AES is larger than that of RCF, it is more irritating to skin, and that it produces more dust since fibers tend to break easily.[2] However, changing the chemical component of AES is difficult because the components have been determined to have AES with low bio-persistence. The fine fiber diameter may allow workers to inhale more fibers. Therefore, remedial measures in which the fiber is directly reformed have not been found. Some researchers have now proposed applying modifying materials to the surface of fibers.[3]

Table 3 Physical properties of AES

	Thermal conductivity (8P-W/m·K) 600°C	1 000°C	Shot (%) +45 μm	Fiber diameter (μm)
Plus	0.12	0.25	35	4.0
HT	0.14	0.34	45	

Table 4 On site qualitative evaluation

Item	On site properties evaluation
Fiber diameter	PCW > AES > RCF
Itching	AES > PCW >> RCF
Dust	AES > RCF > PCW

3. Safety of the High Temperature Insulation Wool to Human Health

3.1 Safety of RCF to human health

Although RCF was widely used as a substitute for asbestos, recently its influence on humans has been seen as a problem. The European Union (EU), which has stricter environmental regulations, has now registered RCF as a substance of high concern. The Japanese government issued a government ordinance (Ordinance No. 294 in 2015) to revise the Industrial Safety and Health Law Enforcement Ordinance in November 2015. In the revised ordinance, RCF among MMVF was categorized as Group-2 special chemical substances. The Japanese government restricted the use of RCF in this revision by demanding companies to take the following measures in the manufacturing and handling of RCF itself and products containing RCF: Installing local exhaust systems; measuring the work environment; selecting workers who manage applicable operations; and providing special medical examinations (the production itself is not prohibited). For operations to attach RCF to ovens and furnaces and to repair, demolish, and crush them, in particular, workers must wear effective protective equipment for breathing and measures to prevent dust from spreading from the work sites must be implemented as obligations.[4] The chemical composition of the target RCF is as follows: Al_2O_3 is 30 to 60 mass%, SiO_2 is 40 to 60 mass%, and RnOm is 0 to 20 mass% (R is Zr or Cr).

3.2 Safety of AES to human health

The development of AES began from a concern over the safety of RCF to human health. In the wake of health impairments caused by asbestos, MMVF started to be evaluated in Europe and the United States due to a concern on the risk of carcinogenicity as was the case with asbestos. The International Agency for Research on Cancer (IARC), which is a subordinate organization under the World

Health Organization (WHO), evaluated the carcinogenicity of MMVF in June 1987. The EU started calling for attention to MMVF in December 1997 through the indication of harm on packages of MMVF. With this trend as an opportunity, MMVF that would be safer to human health started gaining attention and the development of AES began.

3.2.1 Carcinogen categories determined by the IARC

In June 1987, the IARC's working group evaluated the carcinogenicity of MMVF in the wake of health impairments caused by asbestos. MMVF had been further studied since then and in 2001, MMVF was reevaluated to determine the current carcinogen categories. As a result of these two evaluations, RCF was categorized as Group-2B (possibly carcinogenic). For PCW and AES, there is not much carcinogen evaluation data itself and thereby they have not been classified to date.

3.2.2 CLP regulations by the EU

The EU issued EU Directive 97/69/EC "Carcinogen Categories and Indication on Packages for man-made Amorphous Fiber" in December 1997 to instruct that harm be indicated on packages of MMVF to call for attention. The Directive was superseded by the CLP regulations "(EC) No. 1272/2008 Classification, Labeling and Packing of Substance and Mixture" issued in 2008. In the carcinogen categories determined in the European CLP regulations, MMVF types are divided into the two categories shown in **Table 5** depending on the composition: RCF is Category 1B (probably carcinogenic) and glass wool and rock wool are included in Category 2 (possibly carcinogenic). As mentioned previously, there are no standard specifications for AES based on the chemical composition. Therefore, checking whether each AES product type is categorized as Category 2 or 1B is required.

3.3 Low bio-persistent fibers

The aforementioned CLP regulations classify carcinogenicity based on the fiber composition. Fiber types that contain an alkali metal or alkaline earth metal oxide of more than 18% belong to Category 2. The fiber classified as Category 2 is "possibly carcinogenic." The CLP regulations have two exemption requirements from the application of carcinogenicity regarding the fiber types classified as Category 2: Note R and Note Q. For Note Q, the following four requirements are provided. If any of them is satisfied, the fiber is categorized as "Exonerated."

(1) Short-term bio-persistence test by inhalation
Fiber length > 20 μm; half-life of fiber < 10 days
(2) Short-term bio-persistence test by intratracheal instillation
Fiber length > 20 μm; half-life of fiber < 40 days
(3) Intra-peritoneal test
There should be no significant evidence of carcinogenicity.
(4) Long-term inhalation test
There should be no relevant pathogenicity nor neoplastic changes.

Shin-Nippon Thermal Ceramics' AES fiber belongs to Category 2 based on its chemical composition, and it satisfies one exemption requirement. Therefore, it can be defined as a low bio-persistent fiber. It should be noted that such exemption requirements are also applied to rock wool and glass wool in addition to AES. Moreover, since AES fiber is not synonymous with low bio-persistent fiber, it is recommended to check if an AES type is a low bio-persistent fiber before using it. (It has been confirmed that all types of AES that companies participating in Japan High Temperature Inslation Wool Association (JHIWA) sell are low bio-persistent fibers.)

Table 5 Carcinogen evaluation by CLP regulation (Category 2 and Category 1B)

Chemical composition	Category
$Na_2O+K_2O+CaO+MgO+BaO > 18\%$	2 (possibly carcinogenic)
$Na_2O+K_2O+CaO+MgO+BaO \leq 18\%$	1B (probably carcinogenic)

4. Fiber Products and the Development of Application Technologies for the Steel Process

4.1 Fiber products

As methods to manufacture the aforementioned high temperature insulation wool, melting and fibrillization are used for RCF, AES, and other types of amorphous bulk fiber and sol-gel, and fibrillization is used for PCW (crystalline fiber) to produce bulk fiber. To produce blankets, a lubricant is sprayed on fiber, the laminated fiber is processed by needling, and then it is heated to burn the lubricant. Such bulk fiber and blankets are used as raw materials in secondary processing to produce various end products. Z-BLOK has been widely adopted as linings in the steel process. This module product is made by folding a blanket into a pleated shape and combining it with an anchor. Paper, boards, and mold goods are produced by papermaking bulk fibers in the wet process and forming with a mold. Meanwhile, in the dry process, bulk fibers are mixed, twisted, and woven to produce tape, ropes, cloths, and other textile products (refer to **Fig. 1**).

4.2 Main applications for the steel process

The strength of the high temperature insulation wool as heat-insulating materials for the steel process is low, as its fiber structure density is lower than that of other types of fire-resistant materials. Since the specific surface area is large, the high temperature insulation wool reacts easily with components coming from the outside. Due to these characteristics, the high temperature insulation wool is not suitable for applications where it directly comes into contact with molten metal and steel materials. Its main applications are modules for warming covers, heating furnaces, and heat treat furnaces. Other applications are blankets and paper for sealing materials around tundishes, back-up materials for various types of refractories, vacuum formings (VFS), and textile goods for packing for coke ovens.

4.3 Fiber lining

Applications of fiber lining in the steel process are broadly divided into the use for a short period of time and that for an extended period of time. In applications for the use for an extended period of time, technologies to use the high temperature insulation wool as linings were developed to increase the productivity in the steel process and save more energy. In the developed technologies, structure

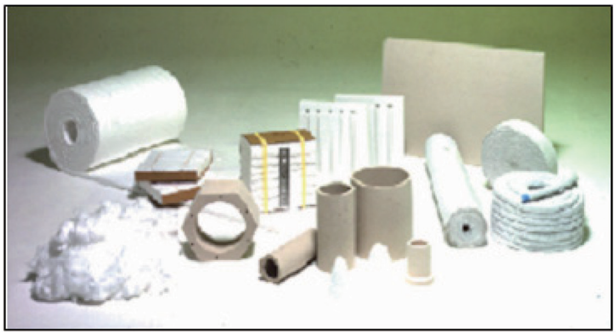

Fig. 1 Various fiber products

and sections for which refractories had been used were replaced with high temperature insulation wool and processed goods made from such wool. In the development, PCW was mainly used. Since the high-temperature shrinkage of PCW is low at approximately 1 500°C and PCW does not embrittle due to crystalline modification, the resilience is characteristically maintained in the high-temperature range. Therefore, PCW is suitable for the use at high temperatures.

4.4 Lining products

4.4.1 Modules (Z-BLOK)

As the shrinkage of modules with PCW is smaller at high temperatures than that of RCF and as the compressive resilience is maintained even at high temperatures, PCW is suitable as linings of heating furnaces. In addition, since the rectangular standard type cannot be used for some heating furnaces depending on their shape, the applicable shape from various types of odd-form modules (e.g., corner, lintel, and two-throw types) has been used in the appropriate place (refer to **Fig. 2**).

4.4.2 Non-water-cooled panel walls

Various odd-form Z-BLOK modules can be produced. One type is non-water-cooled panel walls (called zone dividers) and they have been adopted for heating furnaces. Applying the product is difficult and, in the past, such panels broke and fell off shortly after the start of use. Backgrounds of such problems are elongated panel walls and changes to the operation conditions and environments in furnaces due to the introduction of regenerative burners, which were actively adopted as energy-saving and environmental measures. High-temperature and high-speed elongated flames directly came into contact with walls and severe attacks of scales fanned by high-speed flames

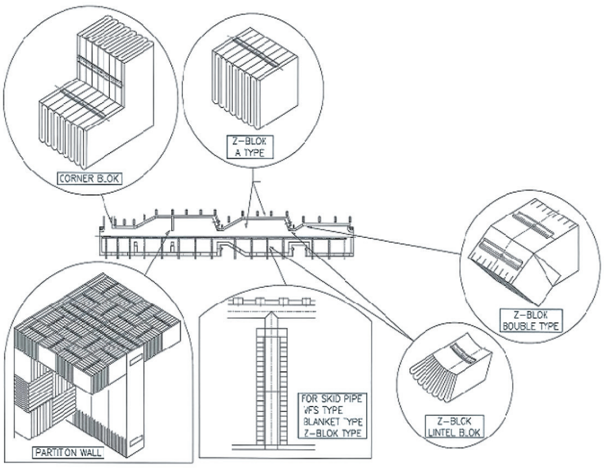

Fig. 2 Various Z-BLOK design

apparently damaged the fiber. After that, the specifications of the PCW blankets (base material) were changed to give high tensile strength at high temperatures and a coating material that has resistance to scales and thermal shrinkage even at high temperatures is applied to the surface of the fiber that directly comes into contact with flames. These measures reduce the risk of the linings falling off (refer to Fig. 2).

4.4.3 Skid supports

For heat-insulating materials for skid supports, although researchers had been trying to apply fiber heat-insulating materials with low thermal conductivity to reduce energy consumption, the durability was a problem. As a solution, vacuum formings (VFS) are used as base materials since the thermal conductivity of VFS is low as is the case with blankets and the finished condition is hard. In addition, the fitting structure was revised: In the new construction method, two divided semicircle parts are used to wrap a skid support like a doughnut to maintain the workability to the conventional level. Using the hard fiber structure as base materials enhanced the hardening and adherence properties of the aforementioned coating material with the resistance to scales and thermal shrinkage, which also enhanced the durability against attacks of scales[5)] (refer to Fig. 2 and **Fig. 3**).

5. Superwool® XTRA

5.1 Development of high-temperature biosoluble fiber

The demand for low bio-persistence AES increased after the RCF regulations were enforced. However, we had only two types of AES products at that time: Those with the classification temperatures of 1 200°C and 1 300°C. Products that would be able to replace RCF for 1 400°C had not been developed. As a result, high-temperature RCF was replaced with PCW, which led to the cost increase. To solve this problem, Superwool® XTRA was developed as a new product type that would be able to be used at high temperatures and that is less expensive than PCW. **Table 6** lists the chemical composition of Superwool® XTRA. Although the chemical composition of Superwool® XTRA in the K_2O-Al_2O_3-SiO_2 system differ from those of AES in the SiO_2-CaO-MgO system, it has been confirmed that Superwool® XTRA is a low bio-persistent fiber. In addition, since the chemical composition of Superwool® XTRA is different from that of AES, some properties of Superwool® XTRA are also different from those of AES.

Table 6 Chemical composition of Superwool® XTRA

	Al_2O_3	SiO_2	ZrO_2	K_2O	MgO
XTRA	36	30	7	26	1

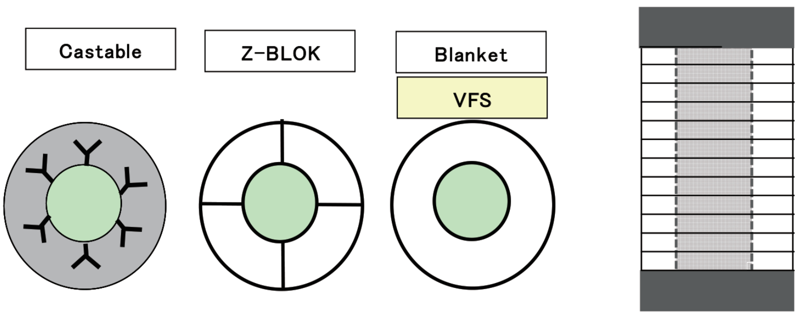

Fig. 3 Cross-section schematic diagram of typical skid support and insulation schematic diagram

5.2 Properties of Superwool® XTRA

5.2.1 High-temperature property evaluation method and results

One factor to evaluate high temperature properties is shrinkage rates for blankets. **Figure 4** shows the shrinkage rates of various amorphous fiber types including Superwool® XTRA. As the test method, each blanket was heated at a designated temperature for a designated period of time and then it was cooled to the normal temperature. The change in the dimensions between before and after heating was used as the shrinkage rate in the quantitative evaluation (the testing procedure is specified in JIS-R 3311, ISO 10635, and other standards).

When the temperature reaches a certain value, the shrinkage rates of amorphous blankets start to deteriorate rapidly. Therefore, the approximate service temperature ranges have been determined as classification temperatures (maximum service temperatures). Figure 4 shows such temperature ranges. Materials were evaluated on the assumption that when they were heated at a designated temperature for 24 hours, the shrinkage rates would be 4% or less. **Table 7** lists the results. A problem is that the shrinkage rate of AES rapidly deteriorates once the temperature exceeds 1200°C or 1300°C. The shrinkage rate of Superwool® XTRA is 4% or less even at 1400°C, and it has been confirmed that Superwool® XTRA has heat resistance at the same level as RCF for 1400°C.

Figure 4 shows that the shrinkage rate of Superwool® XTRA is different from that of the other materials as a property: The shrinkage rate increases at low temperatures. This is caused by fine crystallization of part of XTRA at those temperatures and shrinkage occurred. Meanwhile, the expansion rate of XTRA when the fiber was heated is large. For example, the expansion rate of XTRA is several times larger than that of RCF1400. It has been confirmed that when heated, the contracted clearance is closed (refer to **Fig. 5**). That is to say, at the normal temperature after Superwool® XTRA is heated, the clearance seems larger due to the high shrinkage rate; when reheated, the material considerably expands to close the clearance to retain the heat-insulating properties. It is recommended that Superwool® XTRA modules should be tested and evaluated before application to judge if they can be applied.

5.2.2 Scale resistance

One property of Superwool® XTRA is the scale resistance. As a method to evaluate the scale resistance, an iron plate (FeO) with designated weight was placed on a blanket with a density of 128 kg·m^{-3} as shown in **Fig. 6**. It was heat-treated at the designated temperature for a designated period of time and then the depth of erosion of the iron plate was measured to evaluate the degree of erosion.

Superwool® XTRA shows durability to the erosion of FeO, which has confirmed that its durability is higher than that of AES and PCW (refer to **Fig. 7**).

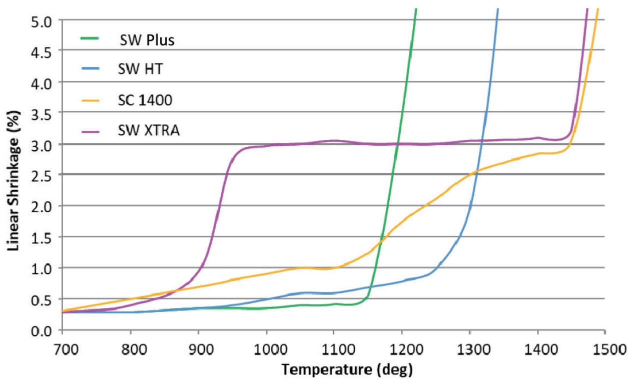

Fig. 4 Shrinkage test heated for 24 hours

Table 7 Shrinkage number (%)

	1100°C	1200°C	1300°C	1400°C
XTRA	3	3.1	3.1	3.5
HT	0.6	0.8	2.3	> 4
Plus	0.3	3.1	> 4	–
SC1400	1	1.7	2.5	2.8

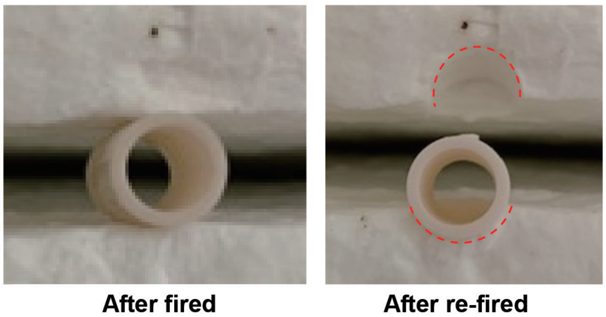

Fig. 5 Evidence of gap closure when re-fired to 1260°C

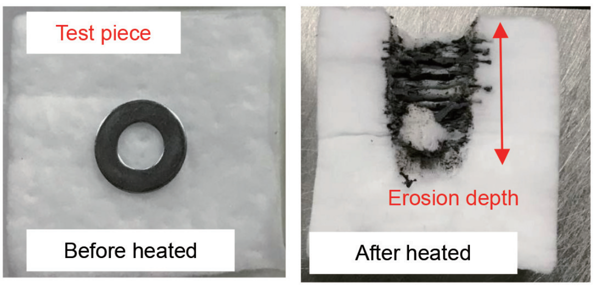

Fig. 6 Example of the FeO resistance test

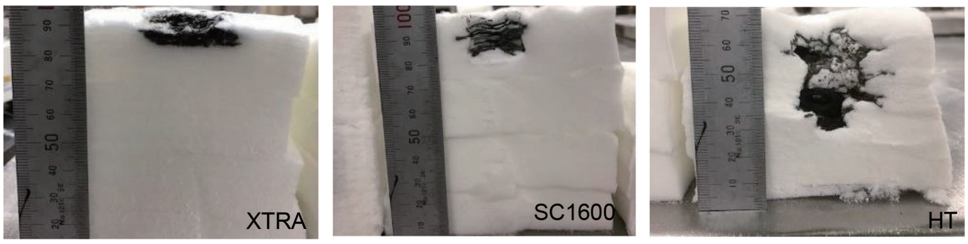

Fig. 7 Picture of FeO resisitance propeties at 1325°C for 5 min with different fiber (XTRA, SC1600, HT)

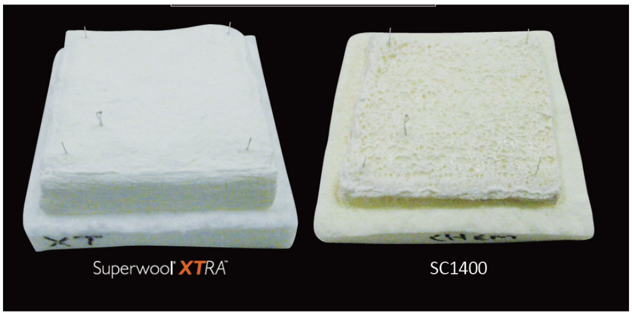

Fig. 8 Alkali resistance evaluation (soaked 3% Na^+ solution and heated 1 300°C for 24 hours)

5.2.3 Alkali resistance evaluation method and results

Superwool® XTRA has alkali resistance compared to RCF. The durability to Na, in particular, surpasses that of conventional RCF1400. The alkali resistance of Superwool® XTRA was compared to that of RCF for 1 400°C in a test in which each type was immersed in a 3% Na^+ solution and then heated at 1 300°C for 24 hours. As clearly shown in **Fig. 8**, Superwool® XTRA has higher alkali resistance than that of RCF for 1 400°C.

5.3 Application to the steel process

Currently, Superwool® XTRA is sold in the forms of blankets and paper (partly bulk, VFS). The application of Superwool® XTRA blankets to the continuous casting process has begun. They were first applied as wrapping materials for submerged and long nozzles, and their excellent durability was verified, which resulted in the adoption. After that, they were adopted as sealing materials for the surrounding of casting equipment in full-scale production. It has been confirmed that the durability of Superwool® XTRA exceeds that of Superwool® HT.

Meanwhile, applying Superwool® XTRA as linings is a future task. For all types of low bio-persistent fibers, there is a concern of crystallization and powdering during heating in the use for an extended period of time, which may weaken the fibers. This may also be true of Superwool® XTRA. As solutions, I would like to make some proposals to steelworks, including the application of reforming materials and coating materials. In addition, for skid supports made from Superwool®, it is uncertain when the development will be completed at present since its high expansion rate may cause cracks in repeated use.

6. Conclusions

Energy-saving technologies that contribute to the prevention of global warming and effective use of fossil fuel will be more important also in the steel industry. The development of heat insulation technologies by Shin-Nippon Thermal Ceramics will be increasingly significant. To improve the steel production process, it is necessary to consider that the process involves harsh conditions for refractories. Considering the safety of MMVF to human health is also an important task from the viewpoint of work environments. Shin-Nippon Thermal Ceramics achieved a certain measure of success in the development of various fiber types for various temperatures through the development of the low bio-persistent fiber Superwool® series. However, there are problems to be solved for the development of use technologies in the steel process. I will continuously work to cooperate with staff engaged in refractory technologies mainly for Superwool® XTRA, which was developed as a material for high temperatures, and will develop more environmentally friendly heat-insulating materials that save more energy.

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