Developments of Zirconia Heating Elements and their Applications to High-Temperature Furnace

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Abstract

Recently, high-tech engineering such as space engineering, requires a high temperature above 2000 ℃ in oxidizing atmosphere. The stabilized zirconia ceramics has been applied to heating elements for high-temperature furnace used in oxidizing atmosphere. Many works concerning the zirconia heating elements have been done mainly in France. However, for actual use and long-life operation, the problems such as thermal spalling and spark phenomena must be resolved. To overcome these problems, new type zirconia heating element composited with zirconia fiber was developed. The investigations have been made in order to construct a high-temperature furnace with long-life employing this newly developed zirconia heating element. The large box type and the cylindrical laboratory furnaces have been accomplished. These furnaces are obtainable high temperature up to 2100 ℃ in oxidizing atmosphere and is durable to 50 heat cycles and continuous run during 500 h.

1 Introduction

It is well known that the zirconia stabilized by doping allovalent oxides has oxygen vacancies, and shows an ionic conduction at high temperatures. Therefore, it is utilized as an oxygen sensor and a solid electrolyte in various fields. The stabilized zirconia has been also applied as a heating element for ten years. A lot of studies concerning the zirconia heating element have been reported, and important problems such as thermal spalling phenomena, creep behavior and spark phenomena occurring at terminal zones have been revealed.[1–5] To overcome these problems, a new type zirconia heating element which is composite of zirconia bulk and zirconia fiber was developed.[6] The investigations have been made in order to construct a high-temperature furnace with long-life employing this newly developed zirconia heating element and the cylindrical laboratory furnace for multi purpose uses was accomplished. This report describes the new type zirconia heating elements and their applications to high-temperature furnace which is obtainable up to 2000 ℃ in oxidizing atmosphere.

2 Developments of zirconia heating element

2.1 Composite with zirconia fiber

For the development of zirconia heating element, it is very important to solve the problems such as thermal spalling and spark phenomena occurring at terminal zones.

To overcome these problems, new type zirconia heating elements composited with zirconia fiber are fabricated. The zirconia fiber was already developed by Shinagawa Refractories Co., Ltd. Physical properties of four kinds of fiber are presented in Table 1. Yttria stabilized zirconia fiber is chosen to composite with zirconia bulk materials to fabricate new type zirconia heating elements. The scanning electron micrograph of yttria stabilized zirconia fiber is shown in Fig. 1. The average diameter of fiber is about 5 μm and the average particle size of fiber is about 0.1 μm.

2.2 Physical properties of zirconia heating elements

Physical properties of new type zirconia heating elements are presented in Table 2. This zirconia heating element is porous material, and its apparent porosity is 27 %. It is considered that this porosity protects the zirconia heating elements from cracking at high temperatures and enables long-life use.

2.3 Electrical resistivity of zirconia heating element at high temperatures

To construct the high-temperature furnace, it is important to measure the electrical reristivity of zirconia heating elements composited with zirconia fiber at high temperatures. The electrical resistivity was measured in the temperature range from 1200 to 1550 ℃ by using the DC two probe method. Cylindrical zirconia heating element having 10 mm in diameter and 100 mm in length was prepared and platium 70 % -rhodium 30 % wire was wound on the the both ends of the heating element. It was put into a furnace and externaly heated in the temperature range from 1200 to 1550 ℃.

The measured temperature dependence of electrical resistivity are shown in Fig. 2 by solid circles. The electrical resistivity of new type zirconia heating element linearly decreases with increasing temperature.

The electrical resistivity above 1550 ℃ was determined from the relationships between applied voltage and flowed current in self-heating of elements having various length of heating zone. Several zirconia heating elements having the same cross section and different length of heating zone were prepared and platinum 70 %-rhodium 30 % wire was wound on the both ends of the heating element. Its schematic diagram and photograph are shown in Fig. 3, 4 respectively. The thin pipes set at both ends of the zirconia heating element are magnesia tubes which prevent the evaporation of the platinum-rhodium wire at high temperatures. After the zirconia heating element was pre-heated by inserting into the hot zone heated by $MoSi_2$ up to 1500 ℃, it was self-heated to the appropriated temperature between 1600 to 2000 ℃ by flowing alternating current. Voltage and current are continuously recorded in heating and cooling tests of heating elements with various length of heating zone and each resistance is determined from relationship between voltage and current. The observed relationship between voltage and current is presented in Fig. 5 for zirconia heating element with heating zone of 10 cm. The electrical resistivity is calculated by using eq. 1.

$$R = (R_1 - R_2)\frac{S}{L_1 - L_2} \tag{1}$$

with

R:electrical resistivity of zirconia heating element
R_1:resistance of zirconia heating element with L_1 cm heating zone
R_2:resistance of zirconia heating element with L_2 cm heating zone
S:cross section of zirconia heating element

The temperature dependence of electrical resistivity of new type zirconia heating element above 1600 ℃ is shown in Fig. 2 by open circles. The electrical resistivity linealy decreased with increasing temperature. The resistivity determined using self-heating method is about 10 % lower than that obtained by extrapolating the resistivity determined using two probe method in the lower temperature region. This difference can be assigned to the temperature gradient in the cross sectional plane perpendicular to heating zone. In the case of self-heating, the temperature of the inside of heating element is higher than the surface temperature because of heat loss from surface. As the specimen temperature indicated in Fig. 2 is measured by optical pyrometer using thermal radiation from surface, mean temperature of heating element is slightly higher than the measured temperature. Therfore, by considering the temperature dependence of resistivity, it is concluded that the mean resistivity of self-heated zirconia heating element is slightly lower than that expected from the measured temperature.

2.4 Physical and chemical property changes after self-heating test

The crystalline phase, chemical composition and density were measured in order to investigate the change of physical and chemical properties of the zirconia heating element after self-heating by current flow. Volume fraction of monoclinic phase of zirconia was determined from X-ray diffraction using the equations proposed by Garrie et al.[7] and Toraya.[8] The crystallite size of zirconia heating element was also determined from X-ray diffraction using Sharrer's equation.[9] X-ray diffraction patterns before and after the self-heating test are shown in Fig. 6 and the determined volume fraction of the crystalline phases and crystallite size are shown in Table 2. Before the self-heating test, the zirconia heating element contains 10 % monoclinic phase in volume fraction. After self-heating test, the monoclinic phase disappears and zirconia is fully stabilized. The destabilization phenomena occurring by evaporation and movement of the stabilizer were not observed.

Chemical composition before and after the self-heating test is shown in Table 4. The amounts of the main compositions such as ZrO_2 and Y_2O_3 did not change, but the content of Na_2O and Fe_2O_3 decreased. From these results, it is considered that the zirconia heating element is stable at high temperatures up to 2000 ℃. The density before and after the self-heating test is shown in Table 4. Apparent porosity decreased about 2 % and the bulk density increased about 0.2 %.

The cycle dependence of electrical resistance of the zirconia heating element during the 50 cycles heating test from room temperature to 2000 ℃ is shown in Fig. 7. The electrical resistance increased about 15 % at the end of heat cycle. The time dependence of electrical resistance of zirconia heating element at 2000 ℃ during continuous heating test of 500 h is shown in Fig. 8. The electrical resistance increased about 5 % at the end of 500 h continuous heating test. The cause for the increase of the electrical resistance is considered to be assigned to the ordering phenomena of oxygen ion vacancies.

From the self-heating test, it became clear that the newly developed zirconia heating element is stable for 50 heat cycles and continuous test during 500 h at high temperatures and it is practically usable to construct the high temperature furnace attainable 2000 ℃ in oxidizing atmosphere.

3 High temperature furnace employed the new type zirconia heating element

Two kinds of high temperature furnace employing the newly developed zirconia heating element were constructed. Their characteristics and applicability are described in the following.

3.1 Large box type high temperature furnace

The structure of box type high temperature furnace is illustrated in Fig. 9. The inside of this furnace is devided into pre-heating space and main heating space by using zirconia refractory materials with good thermal insulation. The $MoSi_2$ heaters are equipped in the pre-heating space and heat externally the zirconia heating elements above 1500 ℃

from which they can be directly heated by flowing alternating current. The 6 to 10 heating elements are equipped in the main heating space depending on the volume of heating space. This furnace is suitable for heat treatment of large volume specimen because large heating space can be provided. The maximum volume of net heating space is 150x150x100 mm^3. The photograph of the box type zirconia furnace is shown in Fig. 10. The temperature of this furnace is controlled by thyristor regulator comparing the programec value with the measured value using optical pyrometer. The temperature stability is ± 5 ℃ at 2000 ℃. The heating rate of 500 ℃/h produces any problem for long-life use. The relationship between obtained temperature and input electric power in box type furnace equipped 6 zirconia heating elements is shown in Fig. 11.

3.2 Cylindrical laboratory furnace for multi purpose uses

Cylindrical laboratory furnace is also constructed for multi purpose uses. This furnace is equipped one cylindrical heating element of 10 to 30mm in inner diameter and 10 to 30 mm in heating zone. The photograph of this cylindrical heating elements is shown in Fig. 12. The thickness of heating zone is thiner than the terminal zones to be effectively heated by increase of electrical resistance. The length of heating zone is selected to fit the desired temperature gradient along cylindrical axis. The cross sectional view of cylindrical laboratory furnace is shown in Fig. 13. The cylindrical zirconia heating element put into the cylindrical space made of stacked zirconia refractory materials. The Kanthal A-1 wire of 1.2 mm in diameter was wound on the outer surface of refractory material and externally heat the cylindrical zirconia heater up to 1100 ℃. Above this temperature, zirconia heating element is self-heated up to 2000 ℃ by flowing alternative current. The photograph of the cylindrical laboratory furnace ia shown in Fig. 14. It is easily recognized that this furnace is compact and is suitable for laboratory use. As only one cylindrical heating element is inserted in the center of the furnace, heating element is easily exchangable and maintenance price is low. The temperature of this furnace is controlled by the same method as that used for the box type furnace. The relationship between temperature and input electric power is shown in Fig. 15. The cylindrical laboratory furnace can be operated with low consumption of electric power. The temperature distribution of the inner space of the cylindrical heating element controlled at 2000 ℃ was measured by W-Re thermo-couple and the obtained result is shown Fig. 16. From these measurements, it become clear that the temperature of the inside is 150 ℃ higher than the surface temprature measured by optical pyrometer for controlling.

This cylindrical laboratory furnace is compact and has a flexibility for multi purpose uses. The possible applications of this furnace are listed in the following.

1. Research and development of ultra-high temperature materials.
2. Sintering and heating test of various ceramics.

3. Growing and annealing of various single crystals.
4. Drawing of optical silica fiber.
5. Melting of glass with high melting point.
6. Ablation test of materials used in space.
7. Quenching and thermal spalling test.
8. Measurements of tensile and breaking strength of ceramics.
9. Creep experiments.
10. Hot pressing.
11. Welding of ceramics with high melting point.

4 Conclusions

Compositing zirconia bulk with zirconia fiber, the new type zirconia heating elements which are stable for thermal spalling phenomena, creep behavior and spark phenomena are developed. From the self-heating test of this heating element, it becomes clear that the considerable changes of their physical and chemical properties for 50 heat cycles and continuous heating during 500 h are not obserbed and they are practically applicable to construct a high-temperature furnace attainable up to 2100 ℃ in oxidizing atmosphere. Two kinds of high-temperature furnace was successfully constructed using the newly developed zirconia heating elements. One is the large box type furnace, the other is the cylindrical laboratory type furnace. The former is suitable for heat treatment of large volume specimen because of its availability of large heating space, the latter is compact and can be heat up to 2100 ℃ by low consumption of electric power. Therefore, the cylindrical furnace is suitable for laboratory use. Its possible applications were examined.

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Table 1. Properties of zirconia fiber.

Code / properties	NZ	C4Z	Y7Z	M7Z
Chemical Composition (wt%)	ZrO_2+HfO_2 99	ZrO_2+HfO_2 95 CaO 4	ZrO_2+HfO_2 92 Y_2O_3 7	ZrO_2+HfO_2 92 7
Crystal Phase	Monoclinic	Tetragonal	Tetragonal	Monoclinic
Appearance	White			
Fiber Diameter	Ave. 5μm			
Fiber Length	Ave.0.5 ~3mm	Ave. 20~30mm		
Melting Point	2600℃			
True Specific Gravity	5.8			
Thermal Conductivity of Y7Z (kcal/m.h. ℃) [W/m.℃]	500 ℃ 1000 ℃ 1500 ℃	0.10 [0.12] 0.26 [0.30] 0.75 [0.87]		0.12 [0.14] 0.17 [0.20] 0.23 [0.27]
	Remarks	When packed with a bulk density of 0.1		When packed with a bulk density of 0.4

Table 2. Typical properties of the zirconia form.

Chemical Composition (%)	ZrO_2+HfO_2 92 Y_2O_3 7
Bulk Density	4.3
Apparent Porosity (%)	27
Modulus of Rupture (kgf/cm²) [MPa]	550 [54]
Crushing Strength (kgf/cm²) [MPa]	900 [88]
Specific Heat (kcal/kg℃) [J/kg℃]	
Thermal Conductivity(kcal/m.h. ℃) [W/m.℃]	0.21 [880] at 2000℃
Thermal Expansion (%)	0.60 [0.7] at 1500℃

Table 3. Crystal phase of zirconia form before and after heating test.

	Crystal Phase	Crystallite Size
Original Zirconia Form	Monoclinic ZrO_2 :90vol% Tetragonal ZrO_2 :10vol%	380 Å
Zirconia Form after Heating Test (Room Temp →2000℃)	Tetragonal ZrO_2 :100vol%	400 Å

Table 4. Chemical composition of zirconia form before and after heating test.

	Chemical Composition (wt%)						
	ZrO_2 +HfO_2	Y_2O_3	CaO	Al_2O_3	SiO_2	Na_2O	Fe_2O_3
Original Zirconia Form	91	7.9	0.1	0.2	0.7	0.1	0.2
Zirconia Form after Heating Test (Room Temp→2000℃)	91	7.9	0.1	0.2	0.7	0.0	0.0

Table 5. Density change of zirconia form before and after heating test.

	Original Zirconia Form	After Heating Test
Dimensional Change (%)	—	− 2.0
Gravity Change (%)	—	− 0.3
Bulk Density	4.3	4.5
Apparent Porosity (%)	27	25

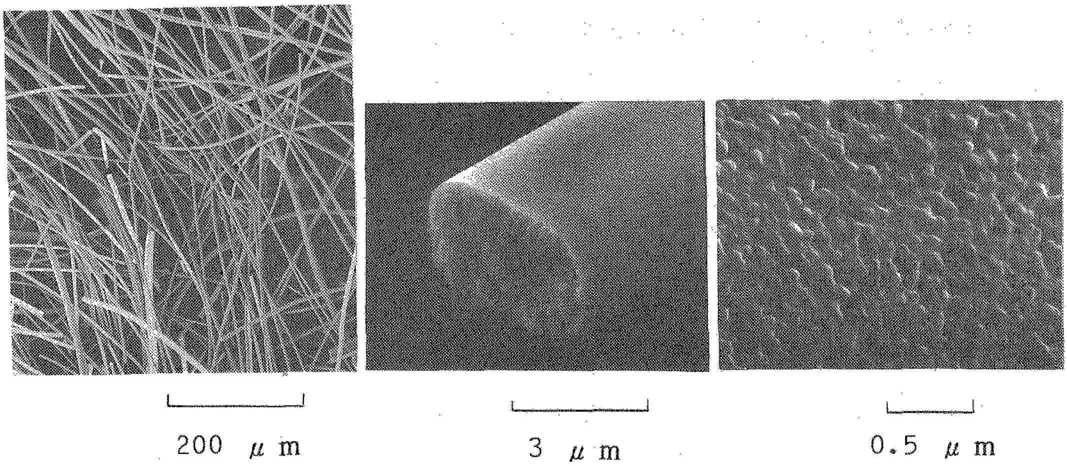

Fig. 1. Scanning electron micrographs of yttria partially stabilized zirconia fiber.

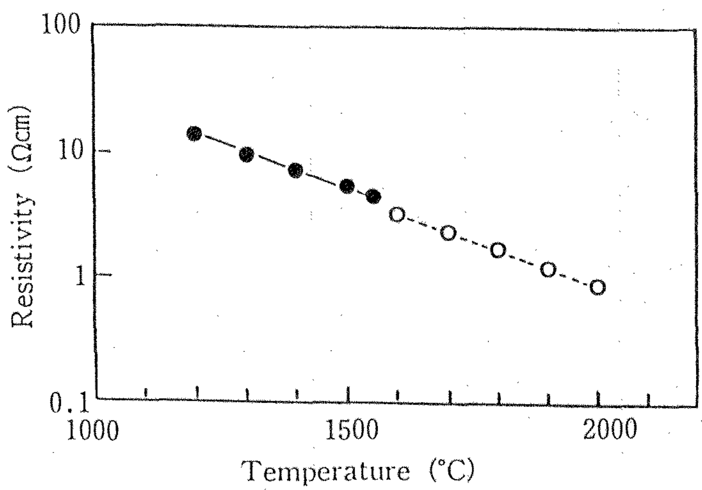

Fig. 2. Temperature dependence of resistivity.
●–●:measured by normal DC two-probe method
○–○:calculated value from the relationship between the voltage and current of the zirconia heating element directly heated by current.

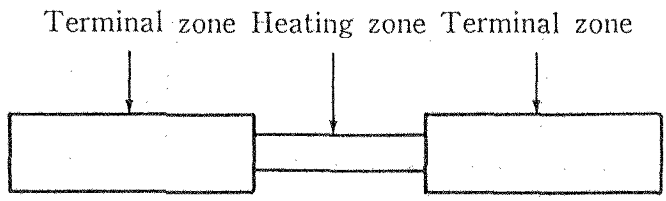

Fig. 3. Schematic diagram of the zirconia heating element.
Terminal zone: ϕ=20 mm, L=60 mm
Heating zone: ϕ=10 mm, L=40,60,80,100,150 mm

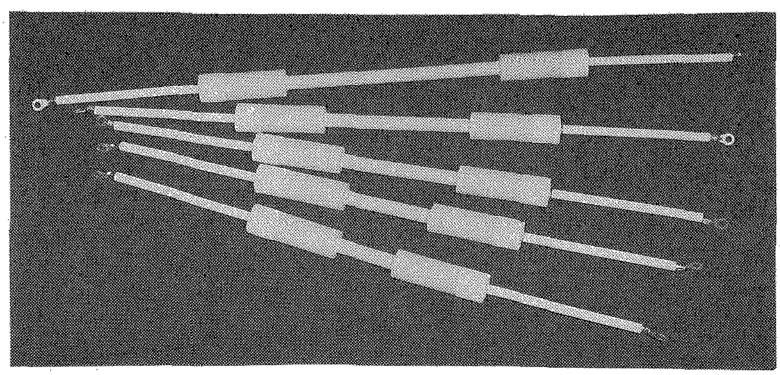

Fig. 4. Photograph of the zirconia forms as a heating element.

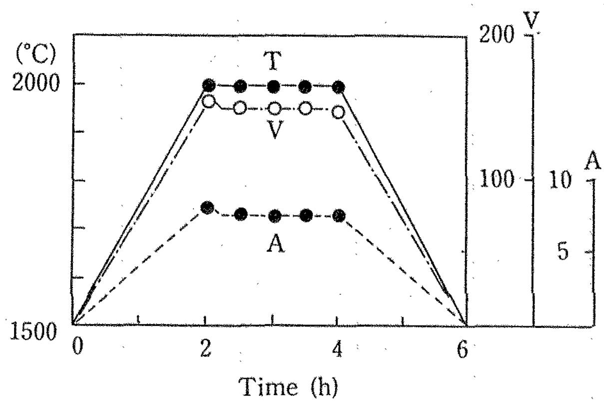

Fig. 5. Heating up diagram and variation of voltage and current of zirconia from.
Length of the heating zone is 100 mm.
T:Temperature(℃), V:Voltage(V) and A:Current(A).

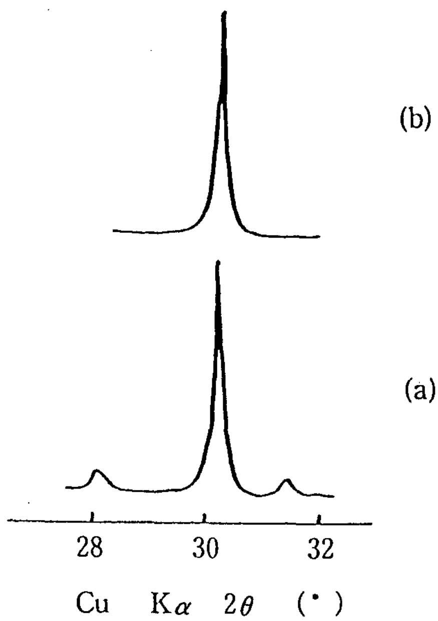

Fig. 6. X-ray diffraction patterns of the zirconia form.
(a)Original (b) After heating.

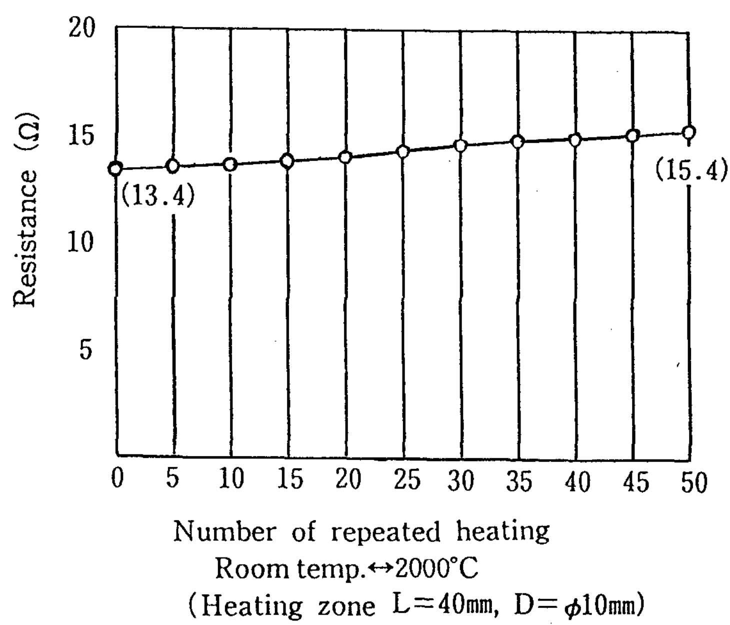

Fig. 7. Electric resistance change of the zirconia heating element in heat cycling test.

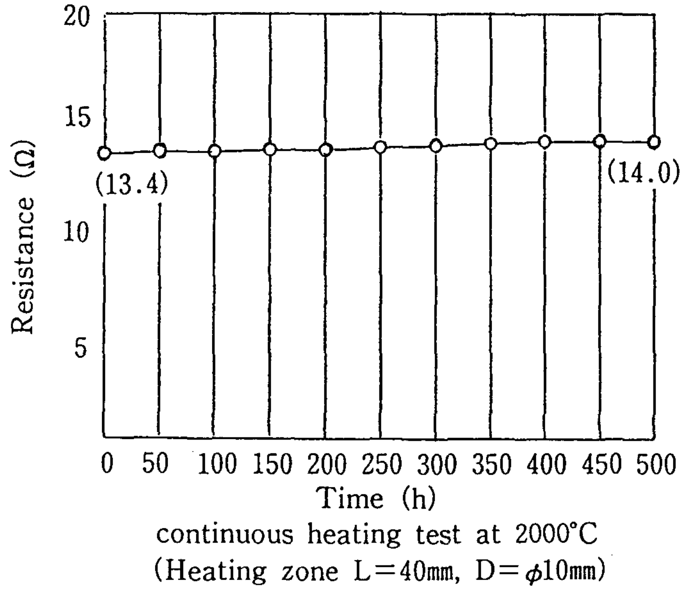

Fig. 8. Electric resistance change of the zirconia heating element during continuous heating.

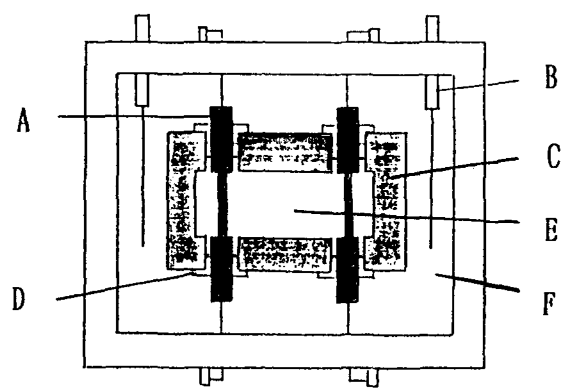

Fig. 9. Cross sectional view of large box type zirconia furnace.
A:Zirconia heating element
B:Pre-heater
C:Zirconia thermal insulator
D:Electric insulating ring
E:Heating room
F:Pre-heating room

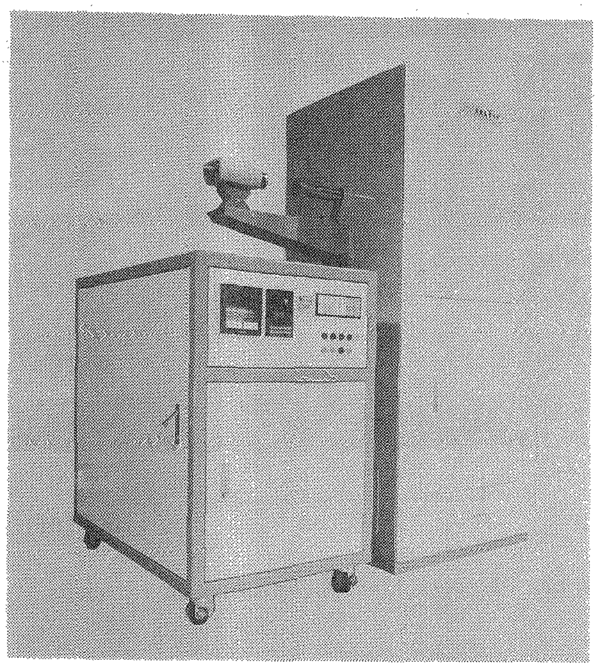

Fig. 10. Photograph of large box type zirconia furnace.

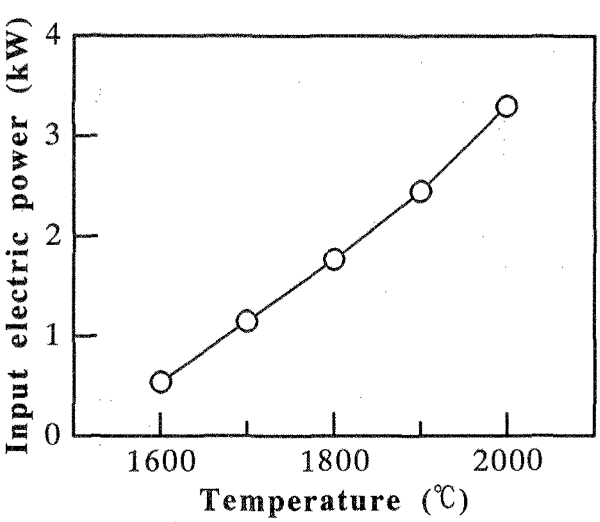

Fig. 11. Relationship between obtained temperature and input electric power of box type furnace using 6 zirconia heating elements.

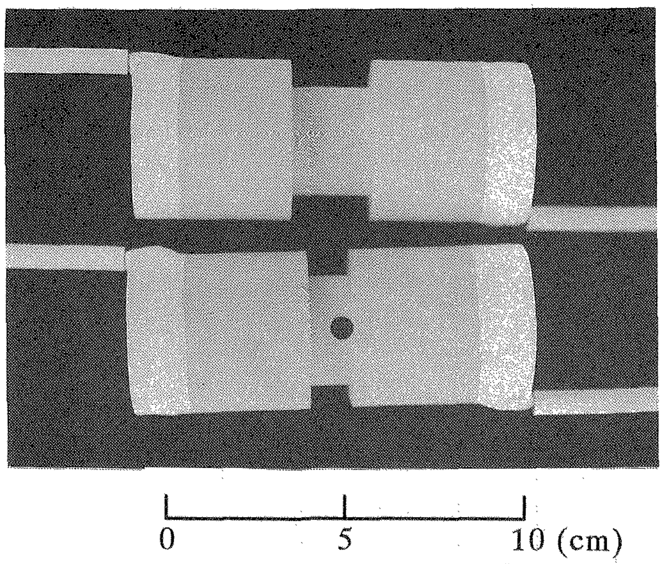

Fig. 12. Photograph of cylindrical heating elements.

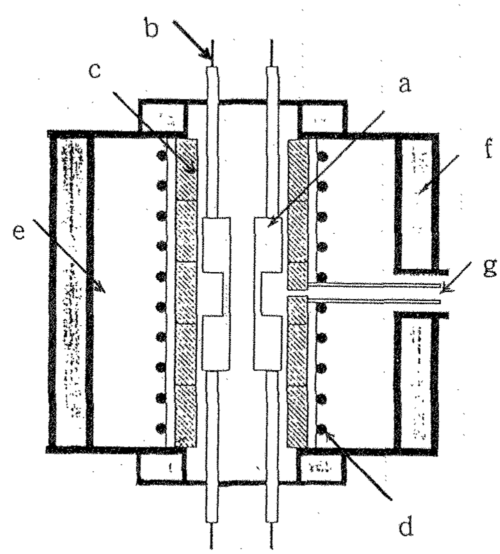

Fig. 13. Cross sectional view of cylindrical laboratory zirconia furnace.
(a):cylindrical heating element
(b):platinum wire for electrical lead
(c):refractory
(d):pre-heater
(e):thermal insulator
(f):metal vessel cooled by circulating water
(g):window for temperature measurement and observation of specimen

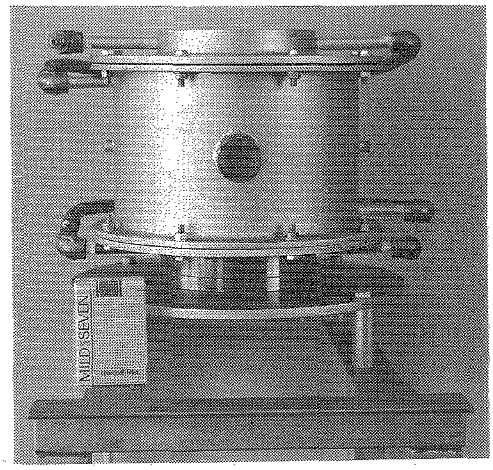

Fig. 14. Photograph of cylindrical laboratory zirconia furnace.

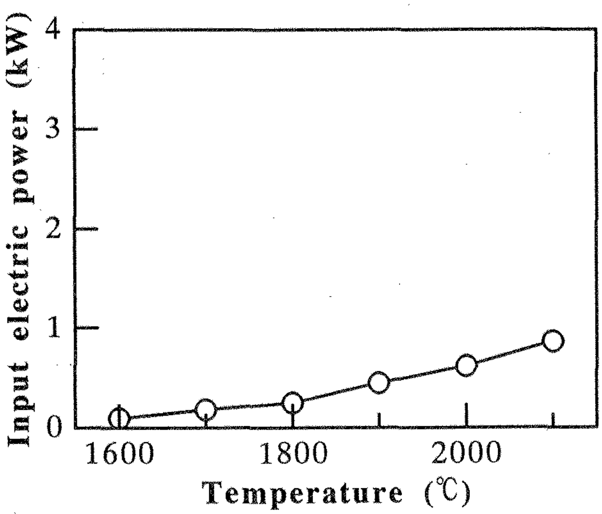

Fig. 15. Relationship between obtained temperature and input electric power for cylindrical laboratory furnace using one cylindrical heating element.

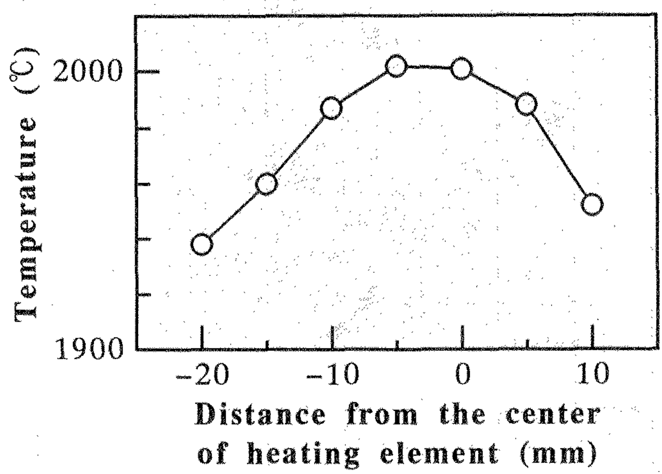

Fig. 16. Temperature distribution of the inner space of the cylindrical heating elememt with 20 mm in heating zone.