

# NEXCERA: Ultra Low Thermal Expansion Ceramics

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## Abstract

*A new design for an ultra low thermal expansion ceramics, "NEXCERA (Naught EXpansion CERAmics)", which shows very low thermal expansion, high specific rigidity and high thermal stability at around room temperature has been successfully developed. This poly-crystalline oxide ceramics achieves virtually zero thermal expansion in this temperature range by controlling the thermal expansion coefficient anisotropy in the crystal. Also, it can be produced by the conventional pressure-less sintering method and it requires no special processing, such as crystallization treatment. In the field of precision and optical instruments, low thermal expansion materials such as Invar alloy and low thermal expansion glass have conventionally been used as the structural members of instruments to avoid dimensional fluctuations due to temperature changes. However, these materials pose some problems, namely inferior rigidity, unstable thermal and mechanical properties and secular changes. NEXCERA is constructed by the newly developed solid solution crystalline without amorphous phase that has solved these problems.*

## 1. Introduction

Generally, all materials, including iron, aluminum, plastics, and ceramics, change in dimensions with changes in temperature. This is because increasing temperature increases the vibration amplitude of atoms comprising materials and hence the spacing between adjacent atoms increases.

In the field of precision equipment and optical equipment that demand a ultra-precision machining accuracy of 1/1,000 of 1 mm or less, low-thermal expansion metals like Invar<sup>1)</sup> and low-thermal expansion glasses<sup>2)</sup> were used to avoid the dimensional change of parts caused by heat. These low-thermal expansion materials are low in specific stiffness (Young's modulus divided by specific gravity), an important property for structural materials, and they change with time<sup>3,4)</sup>. Given these problems, the development of materials capable of achieving high stiffness together with practically zero expansion

or almost no dimensional change with temperature was in high demanded.

Table 1 shows the thermal expansion coefficient, Young's modulus, specific gravity, and specific stiffness of representative industrial materials. Due to their chemical bonding type, covalency, or strong ionicity, advanced ceramics are generally superior in high heat resistance, low specific gravity, high stiffness, low thermal expansion and high chemical stability to metals, glasses and plastics, and have high potential as structural materials. The advanced ceramics listed in Table 1 are low in thermal expansion and high in stiffness as compared with the other materials, and were considered as a material system with the highest possibility of both achieving zero thermal expansion and high specific rigidity.

Since 1985, Nippon Steel Corporation (NSC) has been opening up markets for structural advanced ceramics, and developing prod-

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**Table 1 Thermal and mechanical properties of representative industrial materials at room temperature**

| Material             | Thermal expansion coefficient (ppm/K) | Young's modulus (GPa) | Specific gravity (g/cm <sup>3</sup> ) | Specific rigidity (E/p) (GPa/g/cm <sup>3</sup> ) |
|----------------------|---------------------------------------|-----------------------|---------------------------------------|--|
| Aluminum titanate    | -0.8                                  | 5                     | 3.3                                   | 1.8  |
| Zero-expansion glass | 0.01                                  | 90                    | 2.5                                   | 36.0   |
| Super Invar          | 0.13                                  | 140                   | 8.2                                   | 17.1   |
| Fused quartz         | 0.48                                  | 73                    | 2.2                                   | 33.2   |
| Cordierite           | 0.5                                   | 130                   | 2.5                                   | 52.0   |
| Invar                | 1.2                                   | 144                   | 8.2                                   | 17.6   |
| Sialon               | 1.28                                  | 290                   | 3.2                                   | 90.6   |
| Silicon carbide      | 2.25                                  | 380                   | 3.1                                   | 122.6  |
| Silicon (100)        | 2.54                                  | 170                   | 2.3                                   | 73.9   |
| Alumina              | 5.25                                  | 380                   | 3.9                                   | 97.4   |
| Zirconia             | 6.0                                   | 210                   | 6.0                                   | 35.0   |
| Glass                | 9.0                                   | 70                    | 2.5                                   | 28.3   |
| Carbon steel         | 10.7                                  | 205                   | 7.9                                   | 25.9   |
| Aluminum             | 21.6                                  | 70                    | 2.7                                   | 25.9   |
| Polyethylene         | 150                                   | 0.1                   | 0.9                                   | 0.1  |

ucts to meet various market needs and technologies to manufacture new products. Since our product development efforts focused on "high dimensional stability" by making most of the characteristics of advanced ceramics noted above, we started work on the development of a new ceramic material that realizes zero thermal expansion and high specific rigidity simultaneously.

The following development target values were set meeting market needs:

(1) Ultra-low thermal expansion (thermal expansion coefficient  $\alpha = \pm 0.02$  ppm/K ( $= \pm 0.02 \times 10^{-6}/K$ ), equivalent to thermal expansion of zero-thermal expansion glasses

(2) Specific rigidity ( $E/p > 50$  GPa/g/cm<sup>3</sup>) about 1.5 times higher than that of quartz and glass

(3) Capability of being manufactured by an ordinary ceramic production process composed of forming and sintering

As a result of the above work, we succeeded in developing a ultra-low-thermal expansion material, called NEXCERA\* featured with high specific rigidity, and thus we began to supply this to the market.

This report describes the material design and characteristics of NEXCERA together with the long-time reliability evaluation results of NEXCERA as structural material, and introduces the application development of NEXCERA.

## 2. Theoretical analysis of mixture law for thermal expansion coefficient and elastic modulus

When developing NEXCERA, we first tackled the establishment of a quantitative material design method and theoretically derived a mixture law that considers not only the thermal expansion coefficient but also the elastic modulus and Poisson's ratio by using a composite consisting of two materials as model. We then confirmed principally that there is a structure capable of realizing practically zero thermal expansion and high specific stiffness simultaneously, and

have started developing NEXCERA to verify the theory.

Many models are proposed for the mixture law for the thermal expansion coefficient of composite materials<sup>5-9</sup>. This study attempted the simultaneous estimation of thermal expansion and stiffness by Eshelby's equivalent inclusion method<sup>10</sup> (micro-mechanics theory).

The analysis assumed that heterogeneous inclusions are spherical particles and that the particle/matrix interface will not be detached. The analysis also applied the Mori-Tanaka mean field theory<sup>11</sup> to the effect of particle mutual interference or the effect of particle volume fraction. The detailed analytical procedure is not given here for the lack of space. **Fig. 1** shows the analytical equation of thermal expansion coefficient and analytical solution of thermal expansion coefficient obtained by the analysis.

In the equation,  $\alpha^C$  is the thermal expansion coefficient tensor of the composite material,  $\alpha^M$  and  $\alpha^P$  are the thermal expansion coefficient tensors of the matrix and particles respectively, and  $C^P$  and  $C^M$  are the elastic modulus tensors of the matrix and particles respectively. Each of these tensors can be represented by using Lamé's constants, each of which can be in turn calculated from Young's modulus and Poisson's ratio  $\nu$ . And  $V_f$  is the volume fraction of the particles,  $\tilde{S}$  is the Eshelby tensor when the particles are spherical,  $\tilde{I}$  is the identity tensor of the fourth order, and  $\nu^M$  is Poisson's ratio of the matrix.

It is evident that the thermal expansion coefficient of composite

Analysis of mixture law for thermal expansion coefficient

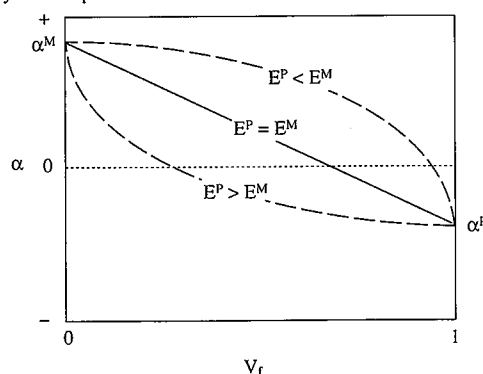
$$\alpha^C = \alpha^M + V_f [A]^{-1} \cdot C^P \cdot (\alpha^P - \alpha^M)$$

where,  $[A] = (C^P - C^M) \cdot [(1 - V_f) \tilde{S} + V_f \tilde{I}] + C^M$

$$\tilde{C} = \begin{bmatrix} \lambda + 2\mu & \lambda & \lambda & & \\ \lambda & \lambda + 2\mu & \lambda & & \\ \lambda & \lambda & \lambda + 2\mu & & \\ & & & 2\mu & \\ & & & & 2\mu \end{bmatrix} \quad \begin{aligned} \lambda + 2\mu &= \frac{(1-\nu)E}{(1+\nu)(1-2\nu)} \\ \lambda &= \frac{\nu E}{(1+\nu)(1-2\nu)} \\ 2\mu &= \frac{E}{(1+\nu)} \end{aligned}$$

$$\tilde{S} = \frac{1}{15(1-\nu^M)} \begin{bmatrix} 7-5\nu^M & 5\nu^M-1 & 5\nu^M-1 & & \\ 5\nu^M-1 & 7-5\nu^M & 5\nu^M-1 & & \\ 5\nu^M-1 & 5\nu^M-1 & 7-5\nu^M & & \\ & & & 8-10\nu^M & \\ & & & & 8-10\nu^M \end{bmatrix}$$

Analysis example



**Fig. 1 Theoretical analytical solution and analytical example of thermal expansion coefficient**

\* NEXCERA is a registered trademark of Nippon Steel Corporation.

materials of a given combination can be estimated by using this analytical solution. From the analytical example in Fig. 1, it can be understood that when particles of minus expansion (or contraction) are dispersed in a matrix of plus expansion, the thermal expansion coefficient of the composite varies significantly according to the level of the difference in the elastic modulus between the dispersed particles and the matrix.

To achieve the combination of zero expansion and high specific stiffness, the purpose of this study, assuming a two-phase dispersion composite, it is found preferable to disperse a small amount of particles with high Young's modulus and minus thermal expansion coefficient, for example. Concrete estimated values can be quantitatively obtained by substituting actual physical properties of the matrix and the particles into the analytical equation.

Theoretical analysis by assuming a two-phase composite was performed. In that process, the developing of several types of zero-expansion ceramics was successful. NEXCERA N113G, featuring zero thermal expansion and the highest stiffness among the new ceramics developed in this study, was expected to have a two-phase separated composition to reflect the results of the theoretical analysis, but was actually a material composed of a single solid solution phase. It is interesting to note that despite the formation of the single solid solution phase, the obtained physical properties agreed well with the theoretically estimated values. This will be taken as a future research issue.

This study analyzed the system in which spherical particles are dispersed. For the results of analysis by Eshelby's equivalent inclusion method of the system where short fibers are dispersed, refer to literature<sup>12, 13</sup>.

The quantitative material design method derived in this study is applicable not only to ceramics but also to metallic materials, and is expected to lead to application development in the future.

### 3. Characteristics of NEXCERA

#### 3.1 Composition and structure

The newly developed material NEXCERA is an oxide ceramic composed only of solid solution crystals where six elements, or lithium, magnesium, aluminum, iron, silicon, and oxygen, are regularly mixed. The solid solution can be substantially represented by the chemical formula  $\text{Mg}_a\text{Li}_b\text{Fe}_c\text{Al}_d\text{Si}_e\text{O}_f$  (a, b, c, d, e, and f range from 1.8 to 1.9, 0.1 to 0.3, 0 to 0.2, 3.9 to 4.1, 6.0 to 7.0, and 19 to 23, respectively).

The general manufacturing flow of this developed material starts with the selection of a raw material blend to meet the chemical composition ranges described above and the preparation of mixed powders. The mixture is then formed, processed before sintering, dewaxed, sintered, machined, and inspected before the product is completed. In actual manufacture, optimum manufacturing conditions must be found by considering the product shape and manufacturing cost. Generally, the uniaxial pressing process with dies or cold isostatic pressing (CIP) process is used for forming, and sintering is performed in the temperature region of 1,200 to 1,500°C. Like general ceramics, this developed material can be sintered by the pressureless sintering process. The crystallization treatment for thermal expansion coefficient control (long-time heat treatment for control of the volume ratio of the crystalline phase in the amorphous phase), required to some zero-expansion glasses, is not necessary.

According to the results of crystalline structure analysis by X-ray diffractometry and the results of microstructural analysis by transmission electron microscopy (TEM), electron probe X-ray

microanalysis (EPMA) with a spot diameter of 10 nm and energy-dispersive X-ray spectroscopy (EDS), the developed material consists of the single crystalline phase (crystalline structure hcp) of the above-mentioned  $\text{Mg}_a\text{Li}_b\text{Fe}_c\text{Al}_d\text{Si}_e\text{O}_f$ , appears as fine grains about 1  $\mu\text{m}$  in diameter, and shows no second phase such as amorphous phase. Fig. 2 shows the typical TEM microstructure of NEXCERA N113G (gray material). Many intragranular dislocations are observed, and the microstructure is also characterized by the small number of pores.

The averaging effect of the thermal expansion coefficient anisotropy described later is predicted to be achieved when an investigation length exceed about 10 crystal grains. Since the crystal grains are small or about 1  $\mu\text{m}$  in diameter, however, virtual zero expansion is considered to be achieved when the evaluation length exceed about 10  $\mu\text{m}$ .

It is generally rare that many dislocations are observed in ceramics. This high dislocation density in each grain is considered to reflect the accumulation of large residual stresses in the crystal grains due to the thermal expansion coefficient anisotropy in the crystal grains. Generally, when there remain large residual stresses in the grains, some micro-cracks spontaneously occur at the grain boundaries as the crystal grains increase in size. In the case of the developed material, since the crystal grain size is small and about 1  $\mu\text{m}$ , the formation of cracks is considered to be inhibited. The mechanism for the formation of square grains waits for future clarification.

#### 3.2 Material design point

The mechanism for the low thermal expansion of the Invar alloy, a representative low-thermal expansion material, is spontaneous volume magnetostriction<sup>1)</sup>. In the case of zero-expansion glass, the required amount of a crystal phase with negative expansion is formed in a glass phase with positive expansion by heat treatment to reduce the thermal expansion coefficient of crystal-glass composite<sup>2)</sup>.

The principal design point of the developed material is not the realization of zero expansion by restricting the vibration of atoms in crystals, but the development of the new material greatly depended on the discovery of new Li-Mg-Al-Fe-Si-O oxide solid solution crystals that expand in some directions and contract in other directions with increasing temperature.

The degree of their expansion and contraction can be controlled within the solid solution range of the composition. When these solid solution particles are sintered into a polycrystalline substance in random directions to offset their expansion and contraction, the macro-



Fig. 2 TEM microstructure of NEXCERA N113G

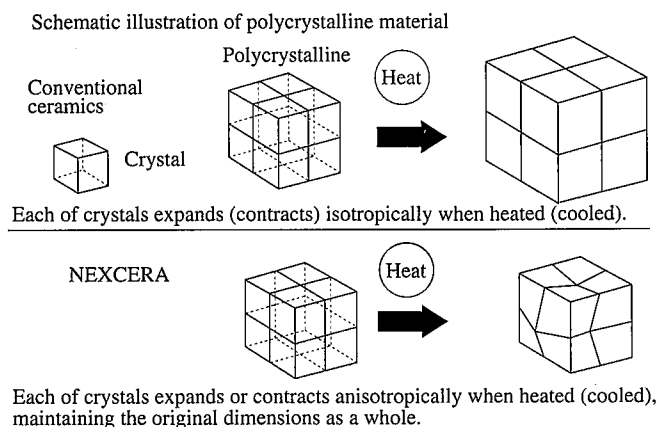


Fig. 3 Schematic diagram of low thermal expansivity of NEXCERA

scopic thermal expansion coefficient anisotropy can be eliminated, and the average thermal expansion coefficient can be made practically zero (Fig. 3). The temperature at which the expansion becomes zero can be continuously changed by changing the composition in the solid solution range. This thermal expansion coefficient anisotropy is being confirmed by measuring the lattice parameter by X-ray diffraction while changing the temperature in the vicinity of room temperature. High specific stiffness is successfully achieved in combination with low thermal expansion by the evolution of a crystal structure of the same system as that of  $\alpha$ -cordierite known to have relatively high stiffness, in addition to the adoption of the solid solution.

The change with age of conventional zero-expansion glasses is considered to result from the coexistence of amorphous and crystalline phases and from the progress with time of the crystallization of the amorphous phase. For this developed material, we selected such a composition that the amorphous phase does not remain. This selection is considered to have improved the thermal stability of the material dramatically and made the material practically free from change in its properties with time.

Many materials have been traditionally known to have the anisotropy of thermal expansion coefficients within crystals, but not many substances combine both of expanding axes and contracting axes<sup>14</sup>.  $\text{NaZr}_2(\text{PO}_4)_3$  and  $\text{Al}_2\text{TiO}_5$  are typical examples of such substances, but their stiffness is extremely low due to the formation of micro-cracks during sintering and cooling. Known as low-thermal expansion materials with relatively high stiffness are  $\beta$ -eucryptite ( $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , thermal expansion coefficient of  $-8$  to  $-2$  ppm/K)<sup>15, 16</sup> and  $\alpha$ -cordierite ( $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ , thermal expansion coefficient of  $0.5$  ppm/K)<sup>17</sup>. However, in these materials, neither combined zero expansion with high specific rigidity.

### 3.3 Properties at ambient temperature

The low-thermal expansion materials call for high accuracy in thermal expansion measurement. This study used a SINKU-RIKO Model LIX-1 laser thermal dilatometer with a Michelson optical interferometer in the precision measurement of thermal expansion coefficients near room temperature, and measured the absolute values of thermal expansion coefficients according to JIS R 3251 concerning the method of measuring the linear thermal expansion coefficient of low-expansion glass by laser interferometry. The specimen geometry was  $14 \times 4 \times 4$  mm, and the edges of the specimen coming into contact with reflecting mirrors for laser interferometry were machined to a diameter of about  $0.1$  mm each to eliminate the effect

of surface condition of the contacts between specimen and mirrors as much as possible. The measurement temperature range was  $-150^\circ\text{C}$  to  $200^\circ\text{C}$ , the heating rate was  $2^\circ\text{C}/\text{min}$ , and helium was selected as measurement atmosphere. The resolution per measurement was  $2$  nm. More than 1,000 data points were acquired in the measurement temperature range and differentiated by fitting with a polynomial equation to achieve a measurement resolution of  $\pm 0.02$  ppm/K or more for thermal expansion coefficients. The thermal expansion coefficient of two specimens was measured for every producing lot, and the obtained values were averaged to determine the thermal expansion coefficient of the developed material.

The representative thermal expansion and contraction curve of the developed material NEXCERA N113G is shown in Fig. 4.

As its thermal expansion and contraction behavior, NEXCERA N113G mildly contracts from the low temperature of  $-150^\circ\text{C}$  to close to room temperature and mildly expands from close to room temperature to the high temperature of  $200^\circ\text{C}$ . It exhibits practically zero expansion in the vicinity of room temperature. The minimal value of the expansion and contraction curve (or the temperature at which the expansion becomes zero) can be controlled in the range of  $0^\circ\text{C}$  to  $40^\circ\text{C}$  by changing the composition of the material. In the case of Fig. 4, the minimum of the curve is  $23^\circ\text{C}$  or the expansion of the material becomes zero at  $23^\circ\text{C}$ . The typical thermal expansion coefficient from  $20$  to  $25^\circ\text{C}$  for N113G is  $\alpha = 0.02$  ppm/K. Fig. 5 shows the curve obtained by differentiating the expansion and contraction curve of Fig. 4 or the thermal expansion coefficient of the material. The ther-

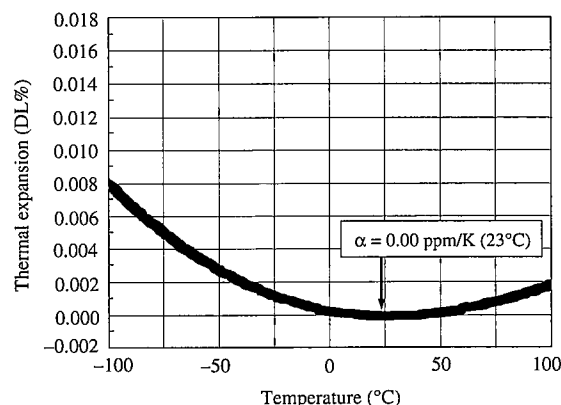


Fig. 4 Thermal expansion and contraction curve of NEXCERA N113G

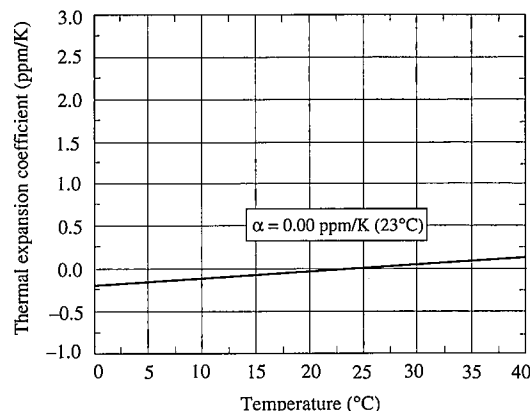


Fig. 5 Temperature dependence of thermal expansion coefficient of NEXCERA N113G

mal expansion coefficient is found to become zero like in Fig. 4.

The dimensional change of the developed material near room temperature is a slight expansion of 0.00002 mm with respect to a temperature rise of 1°C in the case of a 1 m long bar. This expansion is extremely small as compared with representative industrial materials, or is about 1/550 of that of iron, about 1/60 of that of the low-thermal expansion alloy Invar, about 1/24 of that of quartz, about 1/1,100 of that of aluminum, and about 1/7,500 of that of polyethylene.

The specific rigidity of NEXCERA N113G was determined by measuring its Young's modulus by the ultrasonic pulse method specified in JIS R 1602 and its specific gravity by the Archimedes method. Its Young's modulus and specific rigidity were found to be 120 GPa and 51 GPa/g/cm<sup>3</sup>, respectively. The specific rigidity of NEXCERA N113G is 1.4 and 3 times as high as that of commercial low-expansion glass and Invar, respectively. This means that NEXCERA N113G combines extremely low thermal expansion with high specific rigidity.

NEXCERA N113G has few pores when sintered, can be mirror polished, and can be used as mirrors after polishing. The addition of trace elements provides NEXCERA N113G with various colors, including white, gray, green, and black. Its physical properties do not appreciably change with its color.

Fig. 6 shows the thermal expansion coefficients, specific stiffnesses, and typical shaping processes of NEXCERA N113G (gray) and N113 (white), and conventional materials. Table 2 lists the physical properties of the NEXCERA materials in comparison with two zero-expansion glasses. NEXCERA has high bend strength and high thermal conductivity more than twice higher than those of the zero-expansion glasses. A low dielectric constant is its another characteristic.

### 3.4 Elevated-temperature properties

The properties expected for low-thermal expansion materials are not only thermal properties at around room temperature. The ther-

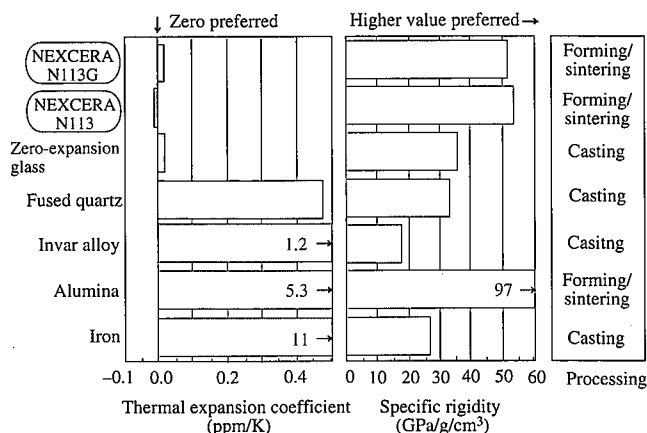


Fig. 6 Thermal expansion coefficient and specific stiffness of NEXCERA N113G and conventional materials

mal expansion coefficient and strength in the elevated-temperature region are indispensable physical properties for structural materials used at elevated temperature.

Fig. 7 shows the thermal expansion curves of NEXCERA N113G and conventional materials. A thermo-mechanical analyzer (TMA) was used for measuring the curves. NEXCERA N113G is found to maintain its low thermal expansion in the elevated-temperature region compared to other materials. Its average thermal expansion coefficient up to 1,000°C is about 2 ppm/K. Fig. 8 shows the elevated-temperature strength of the NEXCERA N113G. The elevated-temperature strength was determined in air by the four-point bend test method specified in JIS R 1604. As evident from Fig. 8, the NEXCERA N113G maintains its strength from room temperature to an elevated temperature of 1,100°C. This suggests the capability of the developed material being used at elevated temperatures of up to about 1,000°C.

Table 2 Physical properties of NEXCERA at room temperature as compared with zero-expansion glasses

| Physical property at room temperature<br>(20 to 25°C)     | N113                 | N113G                | Zerodur               | ULE 7971                  | Test method                        |
|---|----------------------|----------------------|-----------------------|---------------------------|------------------------------------|
|   |                      |                      |                       |                           |                                    |
| Color   | White                | Gray                 | Brown                 | Colorless and Transparent |                                    |
| Specific gravity( $\rho$ ) (g/cm <sup>3</sup> )           | 2.37                 | 2.36                 | *2.53                 | *2.205                    | Archimedes method                  |
| Young's modulus(E) (GPa)                                  | 125                  | 120                  | *90                   | *67.6                     | JIS R 1602 (ultrasonic method)     |
| Poisson's ratio   | 0.31                 | 0.30                 | *0.243                | *0.17                     | JIS R 1602 (ultrasonic method)     |
| Specific rigidity(E/ $\rho$ ) (GPa/g/cm <sup>3</sup> )    | 52.7                 | 50.8                 | 35.6                  | 30.7                      | Calculated from E and $\rho$ above |
| Bend strength (MPa)                                       | 116                  | 185                  | *Approx.50            | *50                       | JIS R 1601 (four-point bend)       |
| Fracture toughness( $K_{IC}$ ) (MPa <sup>1/2</sup> )      | 1.4                  | 1.3                  | 0.8                   | -                         | JIS R 1607 (SEPB method)           |
| Hardness (GPa)  | 7.6                  | 8.1                  | 6.6                   | *4.5                      | JIS R 1610 (Vickers HV10)          |
| Thermal expansion coefficient (ppm/K)                     | -0.01                | 0.02                 | 0.02                  | 0.04                      | JIS R 3251 (laser interferometry)  |
| Thermal conductivity (W/(m·K))                            | 3.64                 | 3.49                 | *1.46                 | *1.31                     | JIS R 1611 (laser flash method)    |
| Thermal diffusivity ( $\times 10^{-6}$ m <sup>2</sup> /s) | 2.00                 | 1.88                 | *0.72                 | *0.79                     | JIS R 1611 (laser flash method)    |
| Specific heat (J/(g·K))                                   | 0.75                 | 0.76                 | *0.8                  | *0.77                     | JIS R 1611 (laser flash method)    |
| Electrical resistance ( $\Omega$ ·m)                      | $2.5 \times 10^{10}$ | $8.8 \times 10^{10}$ | $*2.6 \times 10^{11}$ | $*4 \times 10^9$          | Four-probe method                  |
| Dielectric constant( $\epsilon$ )                         | 4.8                  | 4.8                  | *7.4                  | -                         | Bridge method at 1 MHz             |
| Dielectric loss( $\delta$ )                               | 0.004                | 0.003                | *0.015                | -                         | Bridge method at 1 MHz             |
|   |                      | Schott, Germany      | Corning, USA          |                           |                                    |

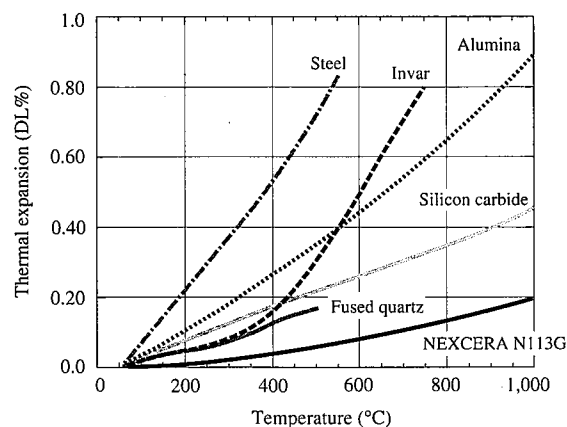


Fig. 7 Elevated-temperature thermal expansion curves of NEXCERA and conventional materials

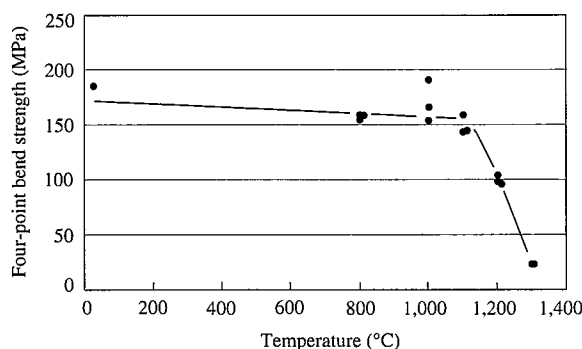


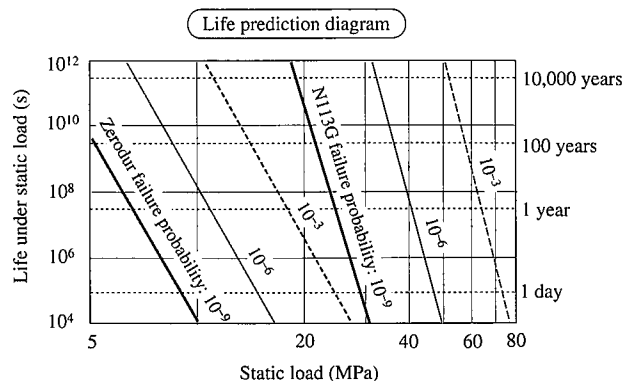
Fig. 8 High temperature strength of NEXCERA N113G

### 3.5 Long-time reliability of mechanical properties

NEXCERA was also evaluated with respect to its long-time reliability as an industrial material. The reliability of mechanical properties was evaluated according to the cumulative failure probability and the fatigue life was predicted under static load. The cumulative failure probability under bending stress was estimated from the failure strength determined by the four-point bend method described in JIS R 1601. The fatigue life under static load was estimated from the stress loading rate dependence of the four-point bend failure strength. In the example of the N113G material, the cumulative failure probability can be represented by a Weibull distribution with the scale parameter  $\sigma_0 = 149$  MPa and a Weibull coefficient of 14.2. Fig. 9 shows a fatigue life prediction diagram based on Weibull statistical processing. The static load under which the cumulative failure probability becomes  $1 \times 10^{-6}$  in  $3 \times 10^9$  s (about 100 years) is more than 30 MPa. The developed material N113G is found to have a fatigue life much longer than that of the conventional low-thermal expansion ceramic materials.

### 3.6 Long-time reliability of thermal expansion coefficient

Accelerated test by heat treatment was conducted for the purpose of investigating the change with time in the thermal expansion coefficient of NEXCERA N113G. The thermal expansion coefficient of NEXCERA N113G did not change with the heat treatment in the temperature range of room temperature to 600°C. This finding verified the capability of NEXCERA N113G to maintain stably its extremely low thermal expansivity for a long period of time. This very small change with time may be attributed to the fact that the developed material consists only of a stable crystal phase and contains no



Effective specimen surface area: 45.3 mm<sup>2</sup>

Surface finish NEXCERA: Ra < 0.2, Zerodur: #100/200 (ASTM) finish\*

\*Value for Zerodur calculated from catalog values of Schott Japan

Fig. 9 Fatigue life prediction diagram of NEXCERA N113G and other materials

unstable amorphous phase.

These long-time reliability evaluation results indicate that NEXCERA N113G is an industrial material with far higher reliability than that of conventional low-thermal expansion ceramic materials and is an extremely promising ceramic as an industrial material for parts requiring high accuracy and high reliability.

## 4. Application Development

NEXCERA is expected to find use in wide applications where high thermal stability is required, including semiconductor manufacturing equipment of which high machining accuracy is required, communication and information industry-related precision equipment, precision tools and jigs, electronic parts, and optical parts. Its expanding utilization is particularly expected in such areas that high stiffness is demanded in addition to low thermal expansion and that zero-thermal expansion glass is cost prohibitive to apply. Fig. 10 shows samples of the ultra-low-thermal expansion ceramic NEXCERA. The upper right white disk is N113, the upper left two gray disks are N113G, and the front right deep gray sample is N113GH or N113G treated to eliminate pores and then mirror polished.

Nippon Steel has already established the NEXCERA mass production and sales promotion system whereby NEXCERA is produced jointly by Nippon Steel and Krosaki Harima, a Nippon Steel Group company, and marketed by Nippon Steel. We will position the

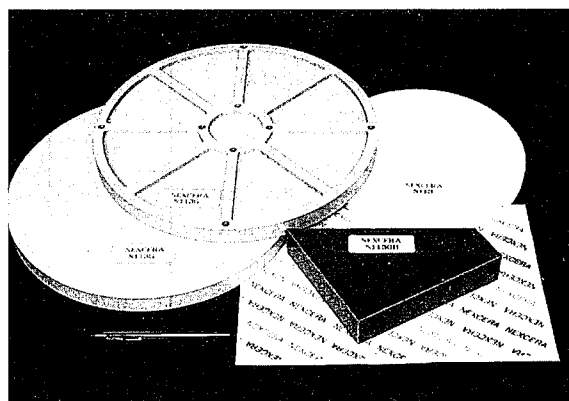


Fig. 10 Samples of ultralow-thermal expansion ceramic NEXCERA

Table 3 Summary of comparison of developed material NEXCERA and conventional technologies

|   | Developed technology<br>NEXCERA N113G   | Conventional technologies<br>1) Zero-expansion glass<br>2) Invar alloy  |
|---|---|---|
| Mechanism of low expansion                          | Polycrystalline material composed only of solid solution crystals consisting of Li-Mg-Al-Fe-Si-O elements (crystal lattice is hexagonal). Anisotropy of thermal expansion coefficient within crystals are controlled by composition | 1) Crystal phase with negative expansion is formed in desired amount by heat treatment in glass phase with positive expansion<br>2) Spontaneous volume magnetostriction is utilized |
| Thermal expansion coefficient (at room temperature) | Practically zero at $\alpha = 0.02$ ppm/K and about 1/60 of that of Invar alloy   | 1) Practically zero-expansion at $\alpha = 0.05$ ppm/K<br>2) $\alpha = 1.2$ ppm/K   |
| Specific rigidity (E/p)                             | 51 GPa/g/cm <sup>3</sup> , about 1.4 times higher than that of zero-expansion glass, and about 3 times higher than that of Invar alloy  | 1) 35 GPa/g/cm <sup>3</sup><br>2) 17 GPa/g/cm <sup>3</sup>  |
| Long-time reliability                               | Static fatigue strength and thermal expansion coefficient stability are more than 10 <sup>8</sup> and 10 times higher than those of zero-expansion glass, respectively, and are estimated not to change with time                   | 1) Change with time<br>2) Change with time  |
| Manufacturing process                               | Low-cost process consisting of powder forming and pressure-less sintering like conventional ceramics  | 1) Casting, crystallization treatment, and machining<br>2) Casting and machining  |
| Coloration  | Trace elements are added to select type of color, such as white, gray or black. No color change   | 1) Amber (no color change)<br>2) Metallic luster (susceptibility to rusting)  |
| Surface morphology                                  | Mirror polishing possible   | 1) Mirror polishing possible<br>2) Mirror polishing possible and rust protection required   |
| Application   | Super-precision, optical, and evaluation equipment  | Precision, optical, and evaluation equipment  |

NEXCERA as one of the main products in our ceramic business and develop the market for the NEXCERA by making use of the overall capability of the Nippon Steel Group.

## 5. Conclusions

The ultra-low-thermal expansion material NEXCERA successfully developed by Nippon Steel has been introduced above. The developed material NEXCERA is compared with conventional technologies in Table 3.

NEXCERA has high specific rigidity in addition to ultra-low thermal expansivity, and also excels in the long-time reliability of thermal and mechanical properties. It is expected as a material to support the technological innovations in the fields of precision equipment and optical equipment.

Further improvements of the properties of NEXCERA will be attempted in an effort to better meet market needs.

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