Journal of Ceramic Processing Research. Vol. 11, No. 6, pp. 721~727 (2010)

J O U R N A L O F
Ceramic Processing Research

Exergy consumption evaluation of a silicon nitride manufacturing process

Hideki Kita*, Hideki Hyuga, Wubian Tian, Takaaki Nagaoka and Naoki Kondo
National Institute of Advanced Industrial Science and Technology (AIST), 2266-98 Shimo-Shidami, Moriyama-ku, Nagoya, 463-8560, Japan

The quality of energy is evaluated by "Exergy". By contrast to the amount of energy preserved, the exergy is irreversibly consumed. The balance of consumed raw materials, energy and exergy in the synthesis process of silicon nitride ceramics that are made from silicon nitride or silicon powder is quantified. The input exergy is reduced by using Si powder as the main raw material with sintering additives of ZrO_2 and spinel. In the manufacturing process of silicon nitride, the majority of the input exergy is consumed in the sintering step. The relationship between the input exergy in sintering step and the sintering temperature, holding temperature as well as the total time is analyzed by a regression method, which gives a guideline for the rationalization of the manufacturing process.

Key words: Silicon nitride, Process, Exergy, Reaction-bonding.

Introduction

Today, energy and environmental issues are becoming serious, and therefore the objective of a manufacturing process is to consume less energy and resources. A similar case exists in ceramics manufacturing. Generally, ceramics are produced by using high-purity and fine powder synthesized artificially as the starting material and sintering at high temperature after forming and dewaxing. Therefore, the input energy for a production process of ceramics is more than those of other materials such as iron and most of the input energy is released finally as heat, resulting in a low utilization efficiency. For the effective applications of ceramic materials in the future, it is necessary to develop manufacturing technologies that consume less resources and energy.

By the way, energy is not consumed but preserved in a closed system according to the first law of thermodynamics. The essence of energy and environmental issues is not about the amount of energy but the deterioration in quality of it. Rationalizing a manufacturing process whilst keeping an eye on the quality of the energy is necessary. The quality of energy is evaluated by "Exergy". By contrast to the amount of energy preserved, the exergy is irreversibly consumed. Moreover, the exergy is a common scale to estimate the resource value of materials and energy. Manufacturing can be interpreted as a system in which the materials and energy are converted into various forms. By using the concept of exergy, we can know the part consumed and amount of material and energy in the manufacturing system. In fact, the exergy is originally used as the standard of heat use efficiency [1]. However, its application for ceramics manufacturing is not available except in our report [2]. To rationalize a manufacturing process of ceramics, the exergy consumption of a specific case is executed here. In this study, the route and amount of exergy consumption during the synthesis process of silicon nitride ceramics are quantified. Based on these results, a new index to measure the amount of resource consumption and a guideline to rationalize the energy-saving synthesis process of silicon nitride are proposed.

*Corresponding author:
Tel : +81-52-736-7232
Fax: +81-52-736-7405
E-mail: hideki-kita@aist.go.jp

Analytical Method

Analytical object

The manufacturing process for obtaining a silicon nitride sintered body was set as an objective. There are two processes using silicon nitride powders as starting materials and two others starting from silicon powders. Among them, the basic process is sintering a compact from a silicon nitride and additive powders mixuture in a nitrogen atmosphere at 1850 °C after forming (hereinafter "Process A"). Then this process was improved based on an exergy analysis.

Silicon nitride plates with a size of 50 × 50 × 5(mm) were made and the weight of consumed material to produce 1 kg silicon nitride plates was measured in each process. The consumed energy was measured with a wattmeter. The necessary data for the exergy analysis related to manufacturing in each process were laboratory ones (e.g., amounts of raw fuel, wasted material and gas as well as water). Tables 1 and 2 show the specifications, models and manufacturers of the raw materials and equipment used in this study.

Table 1. Specifications of materials and milling media used in this study

Main Powder	Si_3N_4 (SN7, Denka) Silicon (#200, Yamaishi Kinzoku)
Additives	Al_2O_3 (AL-1690SG4, Showa Denko) Y_2O_3 (Kinba) Spinel (Syowa Denko) ZrO_2 (TZ-0Y, Toso)
Fluid Media	Ethanol (Koujundo Kagaku)

Table 2. List of equipment

Process	A	B	C	D
Ball Milling	Ball Mill (V-2, Irie Shokai)	←	Planetary Ball Mill (P6, FRITSCH)	←
Granulating	Rotary Evaporater N-N (WATER BATH SB-1000, Tokyo Rika-kikai)	←	←	←
Drying	Over (DV-400, Yamato Kagaku)	←	←	←
Forming	CIP (CL6-20-50, Nikkiso)	←	←	←
Sintering	Sintering Furnace (FVPHP-R-10.FRET-40 Fujidempa Kogyo)	←	←	←

Organization of the system and input/output data

A Manufacturing process is recognized as an assembly of subsystems corresponding to a series of steps. Fig. 1 shows the input/output flow of materials and energy in a manufacturing process. When raw materials and energy are introduced for each step, intermediate products are produced with waste materials and heats that are emitted outside the step. The intermediate product becomes the raw materials for the next step, and the final product is made after a series of steps. To calculate the exergy, it is necessary to know the type and quantity of all raw materials and energies that are introduced into and emitted from the steps, from the starting materials to final product.

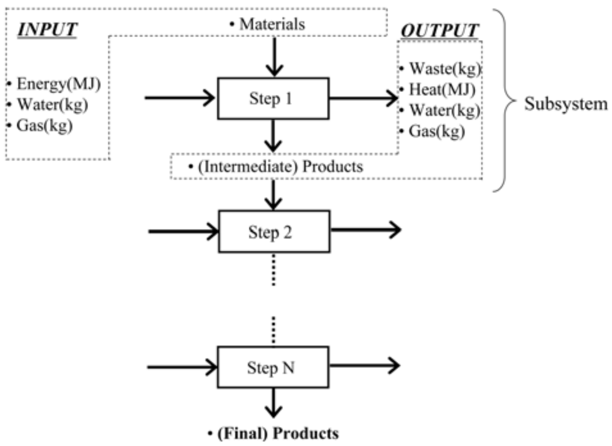


Fig. 1. Input and output flaw of materials and energy in an assembly of subsystems for a manufacturing process.

Analytical methods

① Chemical exergy of matter [3]

If the reference compound with a composition of $X_xA_aB_b$ … (X, A, B are elements; x, a, b are composition ratios), is produced by chemical reaction (1), and the change of Gibbs free energy is ΔG^0, then the chemical exergy E_x^0 can be calculated by equation (2).

$$xX + aA + bB + \cdots \rightarrow X_xA_aB_b \tag{1}$$

$$E_x^0 = \frac{1}{x}[-\Delta G^0 - aE_x^0(A) - bE_x^0(B) - \cdots] \tag{2}$$

Reference material is a matter that does not make a chemical reaction alone in an environment, and its exergy is zero according to the definition of exergy. The exergy of many reference materials are listed in JIS [4], but for the unlisted materials, the lowest free energy is set as that of the reference material.

② Organic material

Although the equations proposed by Rant [1] and Szargut and Styrylska [5] are known for the calculation of chemical exergy of an organic material, the following equation [6] derived from Nobusawa who modified the equations for practical use is applied.

$$Ex = m \cdot H_1 \cdot \left(1.0064 + 0.1519\frac{\phi_H}{\phi_C} + 0.0616\frac{\phi_O}{\phi_C} + 0.0429\frac{\phi_N}{\phi_C}\right) \quad \ldots\ldots \tag{3}$$

m and H_1 are dry mass (kg) and low order heating value (J/kg) of the organic compounds respectively. ϕ_C, ϕ_H, ϕ_O, and ϕ_N are weight fractions of carbon, hydrogen, oxygen, and nitrogen in the organic compound, respectively.

③ Electric power

In the following process, we do not use gas power but only electricity. Electric power does not contain entropy, so it is used directly as the exergy value.

Results and Discussion

Intrinsic exergy

The value of the chemical exergy varies with the selection of reference materials used. Therefore the reference materials need to be described clearly. First of all, the chemical exergies of all the raw fuels and materials are calculated. Table 3 shows the calculated chemical exergies of the raw powders, in which the reference compounds used and the deriving equations are also shown. Here, Ex(Xi) is the exergy of material Xi, and ΔG^0 means the standard Gibbs free energy [7].

Material and energy balance in each process

The idea is to improve manufacturing process and decrease exergy consumption. Overall approaches and sintering conditions are shown in Fig. 2. The detailed explanation is as follows.

Table 3. Calculation of chemical exergy values

Raw Materials	Si	Si_3N_4	$MgAl_2O_4$ (Spinel)	Y_2O_3	ZrO_2
Reference. Materials	SiO_2	SiO_2, N_2 in Air	Al_2O_3	$Y_3Fe_5O_{12}$, Fe_2O_2	$ZrSiO_4$, SiO_2
Chemical Reaction	$SiO_2 \rightarrow Si + O_2$	$Si + (2/3)N_2 \rightarrow (1/3)Si_3N_4$	$Al_2O_3 + MgO \rightarrow MgAl_2O_4$	$(5/3)Fe_2O_3 + Y_2O_3 \rightarrow (2/3)Y_3Fe_5O_{12}$	$SiO_2 + ZrO_2 \rightarrow ZrSiO_4$
Equation for Calculating Exergy	$Ex(Si) = -\Delta G^0 + Ex(SiO_2 - Ex(O_2)$ $Ex(O_2) = RT_0 ln(101.3/20.61$	$Ex(Si_3N_4) = 3\Delta G^0 + 3Ex(Si) + 2Ex(N_2)$ $Ex(N_2) = RT_0 ln(101.3/76.57)$ $Ex(Si) = -\Delta G^0 + Ex(SiO_2) - Ex(O_2)$ $Ex(O_2) = RT_0 ln(101.3/20.61)$	$Ex(MgAl_2O_4) = \Delta G^0 + Ex(MgO) + Ex(Al_2O_3)$	$Ex(Y_2O_3) = -\Delta G^0 + (2/3) Ex(Y_3Fe_5O_{12} - (5/3) Ex(Fe_2O_3)$	$Ex(ZrO_2) = -\Delta G^0 + Ex(ZrSiO_4) - Ex(SiO_2)$
Chemical Exergy (kJ/mol)	851	1877	27	47	5.2

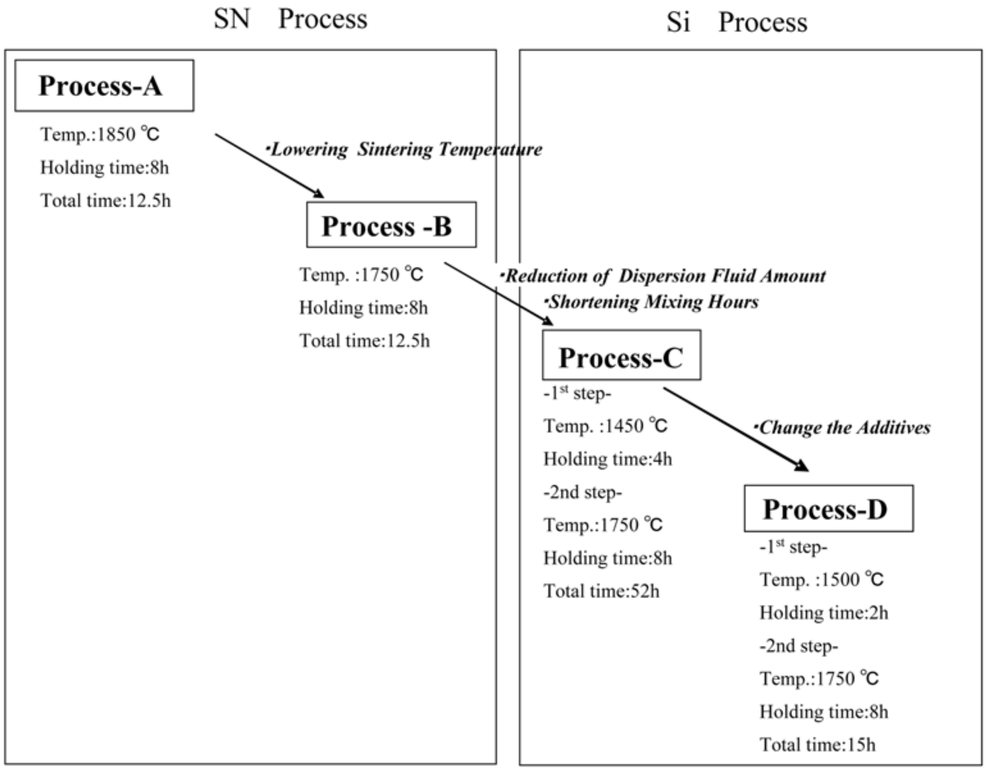


Fig. 2. Overall approaches for rationalization of process and sintering conditions.

① Process A

Processes A and B start from the raw material of silicon nitride powder, as shown in Fig. 2, and process A is the basic one for this study. In process A, starting powders of silicon nitride (90 wt%), alumina (5 wt%) and yttria (5 wt%) are mixed by adding a certain amount of alcohol. After drying, granulating and CIPing (CIP : Cold Isostatic Press), the powder mixture is sintered at 1850 °C in a nitrogen atmosphere to fabricate a silicon nitride sintered body. Table 4 lists the material and energy balance in each process, in which the amount of raw materials, nitrogen gas and consumed electric power to manufacture 1 kg of silicon nitride sintered body is also shown. The loss of raw materials during the milling and granulating steps is about 10%. Therefore, the weights of silicon nitride, alumina and yttria used are 0.99 kg, 0.055 kg and 0.055 kg, respectively. In addition, those of ethanol and nitrogen gas are 1.667 kg and 3.752 kg, respectively. Moreover, the total input energy is 478.971 kWh, in which the sintering step consumes the most, i.e. 410 kWh. On the other hand, it is understood that 5.518 kg raw materials, including nitrogen gas, are abandoned during the synthesis process of 1 kg silicon nitride sintered body.

The exergies of input, wasted and fixed matters in each process were calculated by using the mole exergies of each materials (Table 3) and the actual quantity consumed (Table 4), as shown in Table 5. Process A is evaluated from the viewpoint of exergy consumption as follows.

The input exergy of raw material is 15.582 MJ, in which raw powders occupy 13.245 MJ. The exergy loses by 5% in the following milling and drying steps, and that of the product is fixed at 12.069 MJ (1 kg silicon nitride sintered

Table 4. Materials and Energy Balance for Each Process

		Input		
Materials				(kg)
Si_3N_4	0.990	0.990		
Si			0.595	0.595
Al_2O_3	0.055	0.055	0.055	
Y_2O_3	0.055	0.055	0.055	
ZrO_2				0.055
Spinel				0.055
Ethanol	1.667	1.667	0.961	0.961
N_2	3.752	3.752	15.607	4.502
Sum	6.518	6.518	17.273	6.168
Engery				(kwh)
Process-	A	B	C	D
Ball Milling	15.360	15.360	0.230	0.230
Granulating	5.691	5.691	3.645	3.645
Drying	7.920	7.920	7.920	7.920
Forming	40.000	40.000	25.620	25.620
Sintering	410.000	386.000	1296.000	438.000
Sum	478.971	454.971	1333.416	475.416
		Output		
Products				(kg)
Process-	A	B	C	D
Sum	1.000	1.000	1.000	1.000
Waste Materials				(kg)
Process-	A	B	C	D
Ball Milling	0.050	0.050	0.032	0.032
Granulating	1.383	1.383	0.801	0.801
Drying	0.333	0.333	0.192	0.192
Forming	0.000	0.000	0.000	0.000
Sintering	3.752	3.752	15.248	4.143
Sum	5.518	5.518	16.273	5.168

body). While the exergies of ethanol and nitrogen gas used during sintering are abandoned entirely. The total exergy of wasted materials becomes 3.531 MJ. Then, we discuss the balance of exergy accompanying the energy. First of all, an exergy of 55.296 MJ is input for milling.

In the milling step, it is assumed that a part of the input exergy is used by that of milling. In other steps, it is thought that the input exergy dissipates as heat totally. Here, the entropy S of powder increases during milling, which is determined by calculating the total volume from the density and mixture ratios (assuming that each inorganic compound

Table 5. Exergy Balance for Each Process

		Input		
Materials				kg
Si_3N_4	13.245	13.245		
Si			18.009	18.009
Al_2O_3	0.000	0.000	0.000	
Y_2O_3	0.012	0.012	0.011	
ZrO_2				0.002
Spinel				0.010
Ethanol	2.233	2.233	1.288	1.288
N_2	0.092	0.092	0.384	0.111
Sum	15.582	15.582	19.692	19.419
Engery				(MJ)
Process-	A	B	C	D
Ball Milling	55.296	55.296	0.064	0.064
Granulating	20.486	20.486	13.123	13.123
Drying	28.512	28.512	28.512	28.512
Forming	144.000	144.000	92.242	92.242
Sintering	1476.000	1389.600	4665.600	1576.800
Sum	1724.294	1637.894	4799.541	1710.741
		Output		
Products				(kg)
Process-	A	B	C	D
Sum	12.069	12.069	12.069	12.067
Waste Materials				(kg)
Process-	A	B	C	D
Ball Milling	0.603	0.603	0.805	0.821
Granulating	2.389	2.389	1.863	1.861
Drying	0.447	0.447	0.258	0.258
Forming	0.000	0.000	0.000	0.000
Sintering	0.092	0.092	0.375	0.102
Sum	3.531	3.531	3.301	3.043
Energy				(MJ)
Process-	A	B	C	D
Ball Milling	55.279	55.279	0.048	0.048
Granulating	20.486	20.486	13.123	13.123
Drying	28.512	28.512	28.512	28.512
Forming	144.000	144.000	92.242	92.242
Sintering	1476.000	1389.600	4669.938	1581.139
Sum	1724.277	1637.877	4803.863	1715.064

is dissipated (dispersed) in this volume), the volume fraction and the R × ln (1/volume fraction). In addition, the exergy caused by the increase in entropy during milling is provided by the formula $\Delta S \times 298.15/1000$. The exergy calculated from the entropy of milling is 0.017 MJ. In this study, the entropy caused by the milling step will be included in all of the post-steps.

The input exergies for the granulating and drying steps are 20.486 and 28.512 MJ, respectively. While a part of the raw material is lost and abandoned, and the input electrical power dissipates as heat. Similarly, it is thought that 144 MJ input exergy of the forming step is turned into heat and scattered. The Sintering step inputs and abandons most part of the exergy in the whole process. In process A, the input exergy is 1476.0 MJ when sintered at 1850 °C for 12.5 h. To sum up, the total input exergy in the whole process is calculated to be 1739.876 MJ (The raw material, 15.582 MJ, and energy: 1724.294 MJ).

Then, the output exergy is examined. The exergy of the final silicon nitride sintered body is fixed at 12.069 MJ. The wasted exergies accompanying material and energy (heat) are calculated to be 3.531 MJ and 1724.277 MJ, respectively. From the above calculated results, the second type of efficiency, namely the ratio of the fixed exergy value to the input exergy value, is obtained with a value of 0.67%.

② Process B

The forementioned results of the exergy analysis on process A, i.e. the basic process, show that most of the input exergy is wasted and especially a major part of exergy is input for sintering step. Then, the way to improve the efficiency of manufacturing process is examined. Firstly, we changed the sintering conditions while keeping the others the same as in process A for process B, such as starting powders and forming steps. Compared with process A, the sintering temperature of process B is lower (1750 °C and total time is 12.5 h), and the input energy of necessary electric power is 386 kWh (Table 4). The results of exergy analysis on process B are shown in Table 5. The total input exergy is 1653.476 MJ, where the exergies accompanying raw material and energy are 15.582 MJ and 1637.894 MJ, respectively.

For the energy of the latter, the input exergy for the sintering step is 1389.600 MJ. Additionally, viewing in terms of the exergy, it can be seen that the fixed exergy of the product in the form of silicon nitride is 12.069 MJ and the wasted exergy becomes 1641.408 MJ (The raw material: 3.531 MJ and energy: 1637.877 MJ). The ratio of the fixed exergy value to the input exergy value increases slightly and becomes 0.73%. In processes A and B, silicon nitride powders are used as a starting material. These silicon nitride powders were made by silicon nitridation in a factory of the powder company and at that time energy was also input. In the present study, however, the input energy by the external company is not included in the calculation because our objective is to show the thinking behind the environmental and resource consumption index. For this, we believe that laboratory data could be supportable.

③ Process C

In addition, we think that it is necessary to improve the raw materials, milling step and sintering method to rationalize the manufacturing process. Processes C and D are so-called two-step sintering methods, namely reaction sintering of silicon powder and subsequent densification of the sintered body. For the raw materials, the mole chemical exergy of silicon nitride is 1877 kJ/mol and that of silicon is 851 kJ/mol, where the latter is less than half of the former (Table 3). The necessary raw materials for making a 1 kg silicon nitride sintered body are 0.990 kg silicon nitride or 0.595 kg silicon. The total exergies of the silicon nitride and silicon needed are 13.245 and 18.009 MJ respectively, showing the latter is larger than the former. In Process C, alumina and yttria are used as sintering additives. By this mixture ratio, the weight increases by 1.67 times associated with the reaction between silicon and nitrogen to form silicon nitride in the sintering step. Therefore, the amount of sintering additives can be determined by considering the weight increase during the nitridation process of silicon to form silicon nitride. The mixture ratio of sintering additives in process C is the same as that in processes A and B. It can be seen that the input exergy accompanied with the raw material is 19.692 MJ. Considering the 5% loss of exergy in the following milling and drying steps and fixing the exergy of a 1 kg silicon nitride sintered body at 12.069 MJ, the exergy of the raw powders is 18.020 MJ. In addition, the exergy of ethanol used for milling is abandoned completely. That of the sintering atmosphere of nitrogen is 0.384 MJ, in which the fixed amount is 0.006 MJ and the remainder of 0.376 MJ is wasted. Here, the exergy of nitrogen gas in process C is higher than that in processes A and B. The nitridation and followed sintering are carried out in flowing nitrogen gas, and thus a longer fabrication time is needed and more nitrogen gas is consumed. For the milling step, the exergy of processes A and B is 55.279 MJ and that of process C is 0.048 MJ. This is because the raw powders in Process C are milled by a planetary ball mill for a short time while in processes A and B milling is conducted for a long time with a ball mill. The exergy counted from the entropy of milling is 0.016 MJ, which is smaller than those of processes A and B. This is attributed to the smaller specific weight of silicon than that of silicon nitride. The amount of solvent decreases in process C, and thus the necessary exergy for the granulating and drying steps decreases to 13.123 and 28.512 MJ (41.634 MJ in total), respectively. The exergy for forming decreases to 92.242 MJ due to the shorter time needed.

Concerning sintering, the nitridation is performed at 1450 °C (4 h) and subsequent annealing is carried out at 1750 °C (8 h), total time (52 h) in process C. The electrical power consumed of 1296 kwh, including the necessary electric power for silicon nitridation, is converted into a large exergy of 4665.600 MJ.

The total input exergy for process C is calculated to be 4799.503 MJ (The raw material, 19.692 MJ, and energy: 4779.541 MJ). The output exergy of a silicon nitride sintered body is fixed at 12.069 MJ, which is the same as processes A and B. While the wasted exergy is calculated to be 4819.233 MJ in total (The abandoned materials: 3.301 MJ and the wasted energy as heat: 4803.863 MJ). The fixed ratio of exergy of process C, namely the ratio of the fixed exergy value to the input exergy value, decreases greatly if compared with processes A and B and becomes 0.25%. This result demonstrates that most of the input exergies are abandoned in this process.

④ Process D

It is understood from the analysis of process C that when we use silicon as a starting raw material, the nitridation of silicon to form silicon nitride and the long-time heating in a nitrogen atmosphere will consume a large amount of exergy. Decreasing the input exergy of this process is indispensable to make it rational. In particular, the efficiency of silicon nitridation needs to be improved.

Many authors have studied the nitridation mechanisms of silicon separately. Among them, simultaneous adding of spinel and zirconia is found to be effective to complete the nitridation of silicon at a relatively low temperature in a short time [8]. In Process D, a powder miture of silicon, spinel, and zirconia was used to synthesize silicon nitride. The exergy analysis on this process and the property evaluation of the sintered body obtained was executed.

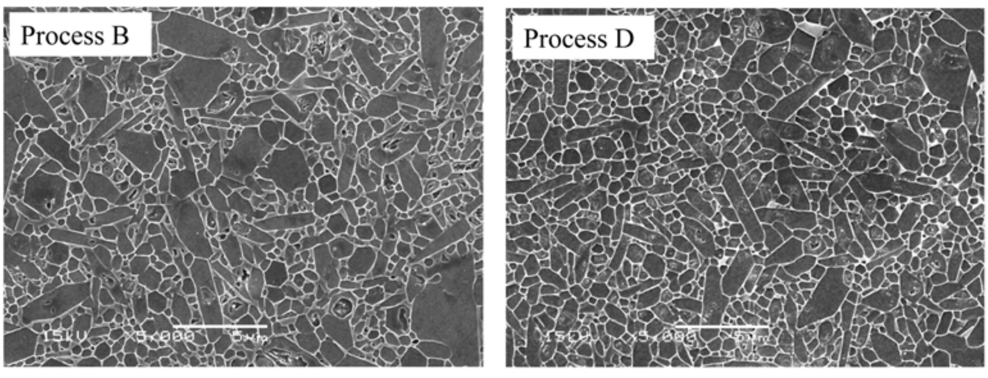
The amount of silicon, spinel and zirconia used is 0.595 kg, 0.055 kg and 0.55 kg, respectively. And that of ethanol and nitrogen gas is 0.961 kg and 4.502 kg, respectively. As described later, the amount of nitrogen gas consumed in process D decreases because the nitridation time becomes shorter as compared with process C. In the milling step, the input exergy is similar to process C. The exergy calculated from the change of entropy during milling is 0.016 MJ. In process D, the sintering step is completed by nitriding at 1500 ºC (2 h) and then annealing at 1750 ºC (8 h). The power consumption decreases to 438 kWh if compared with process C and the corresponding exergy is 1576.800 MJ. Summing up the above results, the input exergy for the whole process is calculated to be 1730.260 MJ in total (The raw material, 19.419 MJ, and energy: 1710.741 MJ). On the other hand, the output exergy of silicon nitride products is fixed at 12.067 MJ, which is slightly smaller than those in processes A, B and C because of the different compositions. The wasted exergy value is 1718.107 MJ (The raw material: 3.043 MJ, heat: 1715.064 MJ). The ratio of the fixed exergy to the input exergy increases slightly to 0.70%.

Characterization of sintered body and guideline of rationalization

Fig. 3 shows the microstructures and properties of silicon nitride sintering body obtained by process B and D. As for the silicon nitride obtained by process B, its strength, σ, is 551 MPa and Weibull coefficient, m, is 13.4. While for process D, the $\sigma = 611$ MPa and $m = 18.1$. Taking the strength and Weibull coefficient into consideration, the sample synthesized by process D is the better one. For comparison, the input exergies of process B and D are 1653.476 and 1736.16 MJ, respectively.

Moreover, it is possible to reduce the input exergy further to be 1538.215 MJ by a rationalized process that is applicable in process B except for the sintering step (The fixed ratio is 0.78% at that time).

However, silicon nitride powder is used as a starting raw material in process B, which is fabricated by nitridation of silicon and subsequent crushing, refinement and classification. The necessary input exergy for synthesizing silicon



Process-	B	D
Fracture strength (MPa)	551	611
Weibull modulus	13.4	18.1
Fracture toughness, K_{IC} ($MPa{\cdot}m^{1/2}$)	4.4	5.1

Fig. 3. Properties of silicon nitride ceramics obtained.

nitride powder is a trade secret and uncertain.

Based on the nitridation experiments in the laboratory, it is thought that at least 1000 MJ is needed for this process and thus a reasonable process to input least exergy is to use silicon as the starting powder, and finish the nitridation and sintering steps in the same process. In addition, the key point to reduce the input exergy is to decrease the necessary exergy for sintering. Based on the above experimental results and regression analysis, an approximate relationship between the input exergy and the sintering time, holding temperature, maximum temperature as well as the total time can be described by the following equation.

$$\text{Input exergy in sintering step} = 0.357 \times \text{sintering temperature}(^{\circ}\text{C}) + 62.472 \times \text{holding temperature} + 85.699 \times \text{total time} - 775.893 \quad (4)$$

Reducing the holding temperature and shortening the sintering time can improve the efficiency of exergy consumption. Developing sintering additives and catalysts for the manufacturing process of ceramics is necessary. Additionally, making a hollow structure with a thinner wall of ceramics products is an effective way to complete sintering in a short time. Moreover, taking the service process into consideration, a very prolonged service life of materials is also effective to decrease the manufacturing frequency and supplementary input exergy.

Conclusions

1) The balance of consumed raw materials, energy and exergy in the synthesis process of silicon nitride ceramics that are made from silicon nitride or silicon powder is quantified.

2) The input exergy is reduced by using Si powder as the main raw material with sintering additives of ZrO_2 and spinel.

3) In the manufacturing process of silicon nitride, the majority of the input exergy is consumed in the sintering step. The relationship between the input exergy in the sintering step and sintering holding temperature as well as the total time is analyzed by a regression method, which gives a guideline for the rationalization of a manufacturing process.

Acknowledgments

This work was supported by New Energy and Industrial Technology Development Organization (NEDO), as part of the Innovative Development of Ceramics Production Technology for Energy Saving project.

References

1. Z. Rant, Forsch. Ing-Wes, 22 (1956) 36-37.
2. H. Kita, H. Hyuga, N. Kondo and T.Ohji, Intl. J. Appl. Ceram. Tech., 5 [4] (2008) 371-381.
3. K. Karakida, “Ekuserugi no kiso”, (Ohm-sya 2005) [in Japanese].
4. Nihon Kogyo Kikaku, Z 9204 (1991) [in Japanese].
5. J. Szargut und T. Styrylska, Brennnst.-Warme-Kraft, 16[12] (1964) 589-596.
6. T. Nobusawa, Nenryou oyobi Nensyou, 43[11] (1976) 49-79 [in Japanese].
7. e.g. MALT, (Kagaku Gijyutu-Sya).
8. H. Hyuga, K.Yoshida, N. Kondo, H. Kita, A. Sugai and H. Okano, J. Tsuchida, Materials Letters 62 (2008) 3475-3477.