Effect of thermal conductivity of ceramic compact on the porous structures of foamed bodies via direct-foaming method

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ABSTRACT
The effect of the thermal conductivity of ceramic compact on the porous structure of a foamed body formed by the direct foaming process was investigated. In order to change the thermal conductivity of the ceramic compact, three types of ceramic powder (alumina, mullite, and cordierite) with different particle sizes were used. These ceramic powders were mixed with powdered resol resin, which is a foamable thermoset resin used as both a foaming agent and binder for the ceramic powders. Ceramic compacts were prepared from the mixed starting ceramic and resol powders by press molding, and then characterized by thermal conductivity. The foamed bodies were produced from the ceramic compacts by heating to the resol foaming temperature to produce porous structures. The pore structures of the foamed bodies were strongly affected by differences in thermal conductivity in the ceramic compacts.

1. Introduction
Porous ceramics have many industrial applications, including uses in refractory components [1], lightweight structural components [2], filters [3], and thermal insulators [4]. Such applications arise from their important characteristics of heat and corrosion resistance, low weights, and high specific strengths. Many studies have investigated fabrication methods for porous ceramics [5–7], including partial sintering, sacrificial fugitives, replica templates, and direct foaming. Among these, the direct-foaming method is low in cost and allows for the easy production of highly porous ceramic materials. During the direct-foaming process, ceramic slurry is generally foamed via gas incorporation; the wet foam is then stabilized, dried, and sintered [8–11]. The stabilization and consolidation mechanisms in this process are of great importance. The ceramic–binder foam is a thermodynamically unstable system in which heat treatment (for drying and debinding) and gas bubble coarsening can degrade and destroy the foam structure. Coarse ceramic powders are widely used in engineering applications, such as refractory components, filters, and thermal insulators, because the coarse particles yield improved creep resistance [12] and thermal shock resistance [13,14] in ceramic components. However, coarse powders are rarely applied for the conventional direct-foaming technique because they precipitate easily from the slurry.

We previously proposed a powder-based direct-foaming method for porous ceramics based on a dry rather than wet process [15]. A schematic of the powder-based direct-foaming method is shown in Figure 1. In the first step, a ceramic compact is prepared from a mixture of ceramic and resin powders by press molding. A thermosetting phenolic resin, which thermal foams upon curing, is used as a foaming agent and binder powder. In the second step, the compact is evenly heated to the foaming temperature of the phenolic resin to produce a foamed body. The foaming gas from the phenolic resin produces uniformly dispersed spherical pores inside the compact, which are then stabilized through the curing reaction between the blowing gas and the phenolic resin. Furthermore, coarse ceramic powders are preferred when using this powder-based direct-foaming method to prepare porous ceramics because the coarse powder particles cannot move easily in the powdery mixture. In the third step, a porous ceramic is obtained by applying a conventional sintering process to the foamed body. The pore structure in the foamed body must be uniform to avoid cracks and defects in the sintered body. Thus, the fabrication of the foamed body is the most important process for the powder-based direct-foaming method in order to produce a porous structure. Because the pore structure is produced by the process of thermally foaming the phenolic resin, the thermal properties of the ceramic compact, especially the thermal conductivity, could be used to control the pore structure. However, the effect of the thermal conductivity of the ceramic compact on the pore structure formation remains unclear.

In this study, three types of starting ceramic powder (starting powder) with different particle sizes, namely high-thermal-conductivity alumina, low-thermal-conductivity mullite, and low-thermal-conductivity
2. Experimental process and characterization

2.1. Experimental procedure

Table 1 summarizes the ceramic powders used in this study. All ceramic powders consist of crushed particles, which means the shapes of the particles are all of an irregular shape. The different particle sizes of alumina powder (Fujimi Incorporated Co. Ltd., Aichi Japan) are referred to as Al-L, Al-M, and Al-S. The different particle sizes of mullite powder (Showa and Denko K.K., Tokyo, Japan) are referred to as Mu-L, Mu-M, and Mu-S. Cordierite powder (Marusu Glaze Co. Ltd., Aichi Japan) is referred to as Co-M. In these names, L, M, and S represent “large,” “medium,” and “small.”

The ceramic powder was mixed with the resol resin powder (Dapor 20 μm, Asahi Organic Chemicals Industry Co. Ltd., Tokyo, Japan) in a plastic pot with iron-cored nylon balls. The mixing ratio of the ceramic to resol powder was 40 to 60 by volume. Each ceramic compact was formed with a diameter of approximately 20 mm and height of approximately 2 mm through press molding. In this molding process, the pressing pressure during molding was adjusted to achieve ceramic compacts of approximately 25% porosity (i.e., with approximate relative density of 75%) to exclude the influence of porosity differences between the ceramic compacts on their porous structures. The porosities of the ceramic compacts were 26% for Al-S and Mu-S compacts and 25% for Al-L, Al-M, Mu-L, Mu-M, and Co-M compacts. For the thermal foaming process, each ceramic compact was placed in a 20-mm diameter plastic tube and heated at 2°C/min to 130°C within 30 min in an electric oven (DK400, Yamato Scientific Co. Ltd., Tokyo, Japan). This heating process yielded foamed bodies.

2.2. Characterization

The thermal conductivities of the ceramic compacts were measured using the heat flow method (EKO HC-110, Eikoseiki, Japan). Thermal analysis of the ceramic compacts was performed in an alumina cell (φ5.5 mm × 4 mm) under air flow through DSC/TG analysis (Q600, TA Instruments, Delaware, USA). Each ceramic compact was cut to fit into the alumina cell for DSC/TG measurement. The pore structures of the compacts and the foamed bodies were observed with an optical microscope (SMZ1500, Nikon Corp., Tokyo, Japan). The average pore size $D_{\text{average}}$ was determined using cross-sectional optical images of the foamed body by the line intercept count method using the equation $D_{\text{average}} = 1.5 \times (L_0/N_{\text{pore}})$, where $L_0$ is the measured pore size and $N_{\text{pore}}$ is the number of pores [16]. At least 100 pores were measured to calculate the average value. The pore-size distributions of the foamed bodies were measured using a mercury intrusion porosimeter (MIP, Autopore 9520, Shimadzu Co, Kyoto, Japan). The Archimedes method, employing vacuum-assisted water infiltration, was used to determine the apparent densities and porosities of the foamed bodies. The morphologies of the ceramic compacts and the foamed bodies were evaluated using a scanning electron microscope (SEM: JSM-5600, JEOL, Japan).

3. Results and discussion

Figure 2 shows cross-sectional scanning electron microscopy (SEM) images with backscattered electrons (BSEs) of the ceramic compacts that used Mu-L, Mu-M, and Mu-S, which means the shapes of the particles are all of an irregular shape. The different particle sizes of alumina powder (Fujimi Incorporated Co. Ltd., Aichi Japan) are referred to as Al-L, Al-M, and Al-S. The different particle sizes of mullite powder (Showa and Denko K.K., Tokyo, Japan) are referred to as Mu-L, Mu-M, and Mu-S. Cordierite powder (Marusu Glaze Co. Ltd., Aichi Japan) is referred to as Co-M. In these names, L, M, and S represent “large,” “medium,” and “small.”

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Figure 2 shows cross-sectional scanning electron microscopy (SEM) images with backscattered electrons (BSEs) of the ceramic compacts that used Mu-L, Mu-M, and Mu-S.
as representative samples. The BSE images provide information about the material composition because heavier atoms (with high atomic numbers) scatter electrons more effectively than lighter atoms (with low atomic numbers). In the BSE images of the ceramic compacts shown in Figure 2, the mullite powder and resin powder appear as the lighter and darker regions, respectively. The mullite and resin powder particles were relatively dispersed in the compact. The mullite particles were in contact with each other in the ceramic compact as a result of the resin powder having a relatively large particle size of 20 μm. The contact of mullite particles were observed regardless of the particle size. Figure 3 shows the thermal conductivities of the ceramic compacts depending on the ceramic powders. The thermal conductivities of the AI-L, Al-M, Al-S, Mu-L, Mu-M, Mu-S, and Co-M compacts were measured at 0.73, 0.62, 0.35, 0.46, 0.30, 0.15, and 0.20 W m\(^{-1}\)°C\(^{-1}\), respectively. The differences in thermal conductivity are attributed to the ceramic types and particle sizes of the ceramic powder. For ceramic powders of different ceramic types but similar particle sizes (Al-M, Mu-M, and Co-M), the thermal conductivity is increased in the order of Co-M → Mu-M → Al-M compacts. The order of the thermal conductivities is the same as that of the thermal conductivities of the dense ceramics (i.e., alumina [40–30 W m\(^{-1}\)°C\(^{-1}\)] \([17,18]\) > mullite [6–5 W m\(^{-1}\)°C\(^{-1}\)] \([19,20]\) > cordierite [3 W m\(^{-1}\)°C\(^{-1}\)] \([21]\)). As Figure 2 shows, the ceramic powder particles were in contact with each other, which indicated that the contacted ceramic particles formed a thermal conducting path in the ceramic compact. Thus, the thermal conductivity of a given ceramic powder could influence the thermal conductivity of ceramic compacts made using that ceramic powder. The use of a ceramic powder with a high thermal conductivity effectively increases the thermal conductivity of the ceramic compact. The thermal conductivity is also changed depending on the particle size of the ceramic powder. The difference in thermal conductivity may relate to the interfacial thermal resistance between ceramic and resin particles in the ceramic compacts. The interfacial thermal resistance blocks heat flow between the ceramic and resin phases because of the differences in the vibrational properties of the different materials \([22]\). The resistance is increased with decreasing particle size because of the increase in the specific surface area of the powder. This particle size effect has also been reported in ceramic–resin composites: the thermal conductivity of ceramic–resin

![Figure 2. SEM images with backscattered electrons of Mu-L, Mu-M and Mu-S ceramic compacts. The lighter regions correspond to mullite particles, and the darker regions correspond to the resin.](image)

![Figure 3. Thermal conductivities of the ceramic compacts: red and black respectively indicate higher-thermal-conductivity compact (HTCC) group and lower-thermal-conductivity compact (LTCC) group.](image)
composites was decreased with decreases in the particle size of the ceramic, even at equal ceramic contents [23–25]. Thus, the thermal conductivities of the ceramic compacts changed depending on the ceramic types and particle sizes of the ceramic powders. The compacts were divided into two groups depending on their thermal conductivities. The first group includes the higher-thermal-conductivity compacts (HTCC) of Al-L, Al-M, and Mu-L, as indicated in red in Figure 3. The second group includes the lower-thermal-conductivity compacts (LTCC) of Al-S, Mu-M, Mu-S, and Co-M, as shown in black in Figure 3.

Figure 4 shows the DSC-TG curves of the ceramic compacts depending on the ceramic types (Al-M, Mu-M, and Co-M, in Figure 4(a) and particle sizes (Mu-L, Mu-M, and Mu-S, in Figure 4(b)). Al-M and Mu-L, as HTCCs, have single exothermic peaks at around 127°C corresponding to large weight losses in the DSC-TG curves. However, Mu-M, Co-M, and Mu-S, which are LTCCs, each have at least one endothermic peak. Mu-M shows a second endothermic peak at a higher temperature. The endothermic peaks of Co-M and Mu-S are broadened toward the higher-temperature side. An exothermic peak at 217°C is observed in all samples and does not change based on the different ceramic powders. An exothermic peak with weight loss is observed in all curves at around 130°C. This exothermic peak is attributed to the curing of the resol resin [26]. The curing mechanism of resol resin involves the condensation of phenol with the methylol phenol unit and the production of a water molecule to form a methylene bridge between the unsaturated rings with crosslink bonding; this has been observed as an exothermic reaction with weight loss [27–30]. The weight loss mainly arises from the evolution of the water vapor as a by-product of the curing reaction. For HTCCs such as Al-M and Mu-L, the foaming occurs relatively uniformly. The LTCCs show exothermic peaks broadened toward higher temperatures. Because the resol resin is a common factor among the ceramic compacts, the endothermic peak assigned to foaming should be observed at the same temperature for all compacts. However, the foaming temperature is shifted higher for the materials with relatively lower thermal conductivities. This indicates that the foaming and curing reactions are prolonged in the LTCCs. Because the DSC/TG equipment measured the temperature of the alumina cell, the measured temperature is almost equal to that of the surface of the ceramic compact. As the temperature evolves, the interior temperature of the compact is increased slowly compared to the surface temperature because of the low thermal conductivity of the ceramics, which enhances the temperature difference between the surface and interior. The interior reaches the foaming/curing temperature later than the surface. Consequently, the foaming/curing reactions inside the compact are delayed compared to those at the outside and the endothermic peak is therefore observed at a higher temperature, causing the splitting or broadening of the exothermic peak. Thus, the foaming behavior is affected by the thermal conductivity of the ceramic compact.

The cross-sectional images of the foamed bodies with the porosity of the foamed body depending on the ceramic powders are shown in Figure 5. The porosity of each sample is shown next to the name of the ceramic powder used in each sample in Figure 5. Cross-sectional images of the HTCC group of Al-L, Al-M, and Mu-L show uniform pore structures. Figure 6 shows an SEM image of the Mu-L foamed body as a representative sample. The foamed pores are spherical in shape and interconnected, yielding an open porous structure. The higher-magnification image shows that the wall structures separating the foamed pores comprise relatively densely packed mullite particles with molten resol resin. The porosities of Al-L, Al-M, and Mu-L are 52%, 43%, and 50%, respectively. Comparing these porosities with the initial porosities of ceramic compacts (ab. 25%), the

![Figure 4](https://via.placeholder.com/150)

**Figure 4.** DSC-TG curves of (A) ceramic compacts with different types of ceramic powders and (B) mullite compacts with different particle sizes.
porosities increased after foaming, which indicates the ceramic compacts of the HTCC group swell during the foaming. The average sizes of the spherical pores of Al-L, Al-M, and Mu-L are 204 μm, 85 μm, and 190 μm, respectively. The pore size distributions of Al-L, Al-M, and Mu-L are shown in Figure 7. These three samples have single distribution peaks located at 89 μm, 35 μm, and 83 μm for Al-L, Al-M, and Mu-L, confirming the uniformity of the pore structures. The average size of the spherical pores from Figure 6 and the peak values shown in Figure 7 differ because the peak value shown in Figure 7 characterizes the diameters of window-like pores, which are the contact points between two spherical pores, rather than the diameter of the spherical pore itself as shown in Figure 6, as previously reported in another study [31]. Thus, when the thermal conductivity of the ceramic compact is relatively high, a uniform porous structure is produced because of the uniform foaming of the resol resin.

The LTCC group of Al-S, Mu-M, Mu-S, and Co-M shows non-uniform pore structures with inside coarse pores in Figure 5. This is especially prominent for Mu-S and Co-M, which showed the lower thermal conductivities of the

| Type of ceramic powder | Alumina | Mullite | Cordierite |
|------------------------|---------|---------|------------|
| Large Particle         | Al-L:52%| Mu-L:50%|             |
| Medium Particle        | Al-M:43%| Mu-M:42%| Co-M:40%   |
| Small Particle         | Al-S:36%| Mu-S:33%|             |

*Porosity of the foamed body was indicated next to the name of ceramic powder

Figure 5. Cross-sectional images of the foamed bodies with their porosity.

Figure 6. SEM image of Mu-L foamed body.

Figure 7. Pore size distributions of Al-L, Al-M, Mu-L, and Mu-M foamed bodies.
ceramic compacts in the LTCC groups as there were large cracks and relatively coarse pores inside the foamed bodies. The porosities of the Al-S, Mu-M, Mu-S, and Co-M foamed bodies are 36%, 42%, 33%, and 40%, respectively. The porosity was increased after foaming, which indicates that the ceramic compacts in the LTCC group swell during the foaming process. The average sizes of the spherical pores without coarse pores around the center are calculated at 31 μm, 80 μm, 29 μm, and 71 μm for the Al-S, Mu-M, Mu-S, and Co-M foamed bodies, respectively. As a representative sample of a foamed body with coarse pores, the pore size distribution of the Mu-M foamed body is shown in Figure 7. The distribution is broadened to include larger pore sizes. As Figure 4 shows in the DSC-TG data, the thermal activation of the resol resin in the LTCCs (Mn-M, Mu-S and Co-M) is broadened toward higher temperatures. The formation mechanism of the non-uniform pore structure is speculated to occur as described below. When the temperature reached the foaming point, the surface of the ceramic compact was foamed and cured to some extent before interior foaming began because of the lower thermal conductivity. The compact weakly resisted expansion as interior foaming began because of the slightly cured surface of the ceramic compact. The foamed pores in the interior were likely to coalesce under this resistance, thus producing coalesced pores inside the foamed body, resulting in the formation of interior coarse pores for Mu-M and Al-S. Meanwhile, the interior pores of Mu-S and Cor-M displayed large cracks rather than the coarse pores. This difference could be related to the lower thermal conductivity of Mu-S and Cor-M compared with Mu-M and Al-S, which caused a further delay of the interior foaming. When the interior foaming occurred, the curing reaction had further proceeded from outer portion to center in the ceramic compact and outer part became relatively rigid because of the curing reaction. The interior foaming produced the large cracks inside the foamed body because the ceramic compact was likely laminated up and down rather than expanded during the foaming.

In addition to the pore distribution, the pore sizes and the porosity of the foamed bodies were also affected by the ceramic powder. The pore size of the spherical pores, except for the coarse interior pores, is increased with an increase in the particle size of the starting powder. The porosity also increased with an increase in the particle size of the starting powder. Although the ceramic types differ, the pore sizes and the porosity remain similar for particles of the same size, such as for Al-M, Mu-M, and Co-M. Differences in pore size and porosity are related to the particle size of the ceramic powder rather than to the thermal conductivity of the ceramic compact. In general, the surface area of the powder is increased with a decrease in particle size. It could be expected that a ceramic powder with a larger particle size would have a lower surface area, decreasing interactions between the ceramic powder and the resin and thus yielding the formation of larger pores during foaming. On the other hand, a ceramic powder with a smaller particle size would have a higher surface area and increased interactions between the powder and resin. The pore formation would be somewhat suppressed by the increased interaction, thus yielding relatively smaller pores.

4. Conclusions

The effect of the thermal conductivity of the ceramic compact on the pore structure of foamed bodies formed using the powder-based direct-foaming method was investigated. Both the ceramic type and the particle size of the ceramic powder affected the thermal conductivity of the ceramic compact. The pore structure was influenced by the thermal conductivity. The foaming behavior of the resol resin was relatively uniform for high-thermal-conductivity precursor powders, resulting in the formation of uniform porous structures. However, relatively lower thermal conductivities caused delays in foaming between the inside and outside of the ceramic compact. Coarse pores were thus produced in the pore structure. Furthermore, the particle size of the ceramic powder also affected the pore size and porosity in the foamed body: the pore size was increased with an increase in particle size. Thus, the present study successfully demonstrated that the thermal conductivity is important in producing ceramics with uniform porous structures using the powder-based direct-foaming method. This suggests that a uniform pore structure could be obtained using various ceramic powders through powder-based direct-foaming by improving the thermal conductivity of the ceramic compact.

Disclosure statement

No potential conflict of interest was reported by the authors.

References

[1] Smith DS, Fayette S, Grandjean S, Martin, C, Telle R, Tonnessen T.. Thermal resistance of grain boundaries in alumina ceramics and refractories. J Am Ceram Soc. 2003 Jan;86(1):105–111.
[2] Colombo P. Conventional and novel processing methods for cellular ceramics. Philos Trans R Soc London A. 2006 2006-01-1500:00:00;364(1838):109–124.
[3] Topateş G, Petasch U, Adler J, et al. Production and permeability of porous Si3N4 ceramics produced by starch addition. J Asian Ceram Soc. 2013/09/01/;1 (3):257–261.
[4] Fukushima M, Tsuda S, Yoshizawa Y-I. Fabrication of highly porous alumina prepared by gelation freezing route with antifreeze protein. J Am Ceram Soc. 2013;96 (4):1029–1031.
[5] Ohji T, Fukushima M. Macro-porous ceramics: processing and properties. Int Mater Rev. 2012;57(2):115–131.
[6] Studart AR, Gonzenbach UT, Tervoort E, et al. Processing routes to macroporous ceramics: A review. J Am Ceram Soc. 2006;89(6):1771–1789.

[7] Eom J-H, Kim Y-W, Raju S. Processing and properties of macroporous silicon carbide ceramics: A review. J Asian Ceram Soc. 2013;9(3):220–242.

[8] Barg S, Soltmann C, Andrade M, et al. Cellular ceramics by direct foaming of emulsified ceramic powder suspensions. J Am Ceram Soc. 2008;91(9):2823–2829.

[9] GU T, SA R, Elena T, et al. Macroporous ceramics from particle-stabilized wet foams. J Am Ceram Soc. 2007;90(1):16–22.

[10] Mamata P, Parag B. Effect of sucrose on fabrication of ceramic foams from aqueous slurries. J Am Ceram Soc. 2005;88(1):216–218.

[11] Vijayan S, Wilson P, Prabhakaran K. Porosity and cell size control in alumina foam preparation by thermo-foaming of powder dispersions in molten sucrose. J Asian Ceram Soc. 2016;89(6):1771–1789.

[12] Kingery WD, Bowen HK, Uhlmann DR. Introduction to ceramics. New York: Wiley; 1976.

[13] BA P, LB A, OCB H. Resistance of alumina-spodumene ceramics to thermal shock. J Am Ceram Soc. 1999;82(4):819–824.

[14] Wang L, Shi J-L, Chen H-R, et al. Effect of size of the starting powders on the thermal shock resistance of alumina ceramics [journal article]. J Mater Sci Lett. 2001 February 01;20(4):341–342.

[15] Shimamura A, Fukushima M, Hotta M, et al. New processing approach for macro porous RB-SiC derived from SiC/novolac-type phenolic resin by direct foaming. J Ceram Soc Japan. 2016;125(1):7–11.

[16] R1601 JIS. Testing method for grain size in microstructure of fine ceramics. Japan Standards Association.

[17] Morrell R. Handbook of properties of technical & engineering ceramics. Section I. High-alumina ceramics. London: H.M.S.O; 1987.

[18] Kingery WD. Thermal conductivity: XII, temperature dependence of conductivity for single-phase ceramics. J Am Ceram Soc. 1955;1855/07/01:38(7):251–255.

[19] Torrecillas R, Calderón JM, Moya JS, et al. Suitability of mullite for high temperature applications. J Eur Ceram Soc. 1999;1999/10/01;19(13):2519–2527.

[20] Hirata Y, Shimonosono T, Itoh S, et al. Theoretical and experimental analyses of thermal properties of dense polycrystalline mullite. Ceram Int. 2017;2017/09/01:43(13):10410–10414.

[21] Li Y, Wang J, Wang J. Approaching extremely low thermal conductivity by crystal structure engineering in Mg2Al4SiO18. J Mater Res. 2015;30(24):3729–3739.

[22] Pietrak K, Wiśniewski TS. A review of models for effective thermal conductivity of composite materials. J Power Technol. 2015;95(1):14–24.

[23] Chung SL, Lin JS. Thermal conductivity of epoxy resin composites filled with combustion synthesized h-BN particles. Molecules. 2016;21(5):May.

[24] Devpura A, Phelan PE, Prasher RS. Size effects on the thermal conductivity of polymers laden with highly conductive filler particles. Microscale Thermophys Eng. 2001;5(3):177–189.

[25] Ishida H, Rimdusit S. Very high thermal conductivity obtained by boron nitride-filled polybenzoxazine. Thermochim Acta. 1998;99(1102):320(1):177–186.

[26] Lee YK, Kim DJ, Kim HJ, et al. Activation energy and curing behavior of resol- and novolac-type phenolic resins by differential scanning calorimetry and thermogravimetric analysis. J Appl Polym Sci. 2003;89(10):2589–2596.

[27] Park BD, Riedl B, Kim YS, et al. Effect of synthesis parameters on thermal behavior of phenol-formaldehyde resol resin. J Appl Polym Sci. 2002;83(7):1415–1424.

[28] Byun HY, Choi MH, Chung U. Synthesis and characterization of resol type phenolic resin/layered silicate nanocomposites. Chem Mater. 2001 Nov;13(11):4221–4226.

[29] Knop A, Pilato LA. Reaction mechanisms. phenolic resins: chemistry, applications and performance future directions. Berlin, Heidelberg: Springer Berlin Heidelberg; 1985. p. 24–61.

[30] Mitchell SJ, Pickering RS, Thomas CR. The effect of phenol/formaldehyde ratio on the char yield from phenolic resins. J Appl Polym Sci. 1970;14(1):175–183.

[31] Shimamura A, Fukushima M, Hotta M, et al. Fabrication and characterization of porous alumina with denser surface layer by direct foaming. J Ceram Soc Japan. 2017;125(1):7–11.