

利用高频交流电提高闪烧均匀性：趋肤效应的作用

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摘 要: 闪烧技术自发现以来已经被广泛研究了 10 多年, 但其实际应用却极少被讨论, 闪烧应用的主要挑战是烧结大尺寸样品时的困难。在典型直流电闪烧中, 电流主要集中在样品的中心, 样品内部和表面之间存在显著的温度梯度, 导致最终样品的微观结构不均匀, 甚至样品中的内应力会致使样品开裂。本工作利用不同频率的交流电来研究频率对闪烧中这种不均匀性问题的影响。结果表明, 增加频率显著提高了样品的均匀性, 其原因主要是由于交流电闪烧中存在显著的“趋肤效应”, 即电流密度集中在样品的表面而不是样品中心, 这补偿了表面较高的辐射热损失, 从而导致更均匀的样品温度。本工作提供了一种潜在的方法, 可以显著提高闪烧在工业领域的实际应用。

关键词: 交流电闪烧; 微观结构均匀性; 趋肤效应

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Enhancing Uniformity in Flash Sintering Through High-Frequency Alternating Current - Role of Skin Effect

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Abstract: Flash sintering is extensively investigated for over a decade since its discovery, but its practical application is seldomly discussed. A primary challenge in utilizing flash sintering is a difficulty in sintering large samples. This is since in a typical direct current (DC) flash sintering, the current is concentrated primarily in the center of the sample, causing a significant temperature gradient between the interior and surface of the sample, thus leading to an inhomogeneous microstructure in the final product and sometimes large stresses in the sample that breaks the material. In this paper, we utilized the alternating current (AC) with varying frequencies to investigate its effect on this inhomogeneity issue in flash sintering. The results indicate that increasing the frequency significantly enhances the uniformity of the sample. The underlying mechanism is related to a significant “skin effect” in AC flash sintering, where the current density is concentrated on the surface of the sample rather than its center, compensating for a higher radiation heat loss at the surface and resulting in a more uniform sample temperature. This work provides a potential approach to enhance the flash sintering for industrial applications.

Keywords: alternating current flash sintering; microstructure homogeneity; skin effect

1 Introduction

Flash sintering (FS) is an efficient electric field-assisted sintering method that has been extensively

researched in the past decade^[1-6]. This method can be used to completely sinter materials in just a few seconds and at a much lower furnace temperature than conventional sintering methods^[1]. Its potential applications

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in the production of ceramic^[7] and metal^[8] materials make it a promising technique for industrial use. However, obtaining a large sample size through flash sintering remains a bottleneck due to the large temperature difference between the sample center and surface^[9–10]. The temperature difference is mainly caused by the heat dissipation through radiation and convection at the sample surface. The uneven temperature will lead to uneven sample microstructure, typically a much larger grain size in the sample core compared to that close to the sample surface^[11], and in the worst cases even cracking of the material^[12–13]. Therefore, a critical issue that needs to be solved for the practical application of FS is to improve the homogeneity of temperature distribution, especially between the sample surface and core.

Carvalho *et al*^[14] found that the AC flash sintered (FSed) sample had larger grains near the surface compared to the center and attributed this phenomenon to the so-called “skin effect”. In electromagnetism, the skin effect is the tendency of an AC to become distributed within a conductor so that the electric current flows mainly at the “skin” of the conductor, between the outer surface and a level called the skin depth. Although this work has implied that it might be possible to balance the lower temperatures at the sample surface in the case of normal DC FS with a higher current density in the AC condition, no systematic investigation on this effect has been carried out.

Therefore, this work aimed to assess the impact of AC frequency on the grain size distribution of FSed samples to evaluate whether AC FS can be an effective approach for improving microstructural homogeneity. The cross-section of samples was analyzed using scanning electron microscopy (SEM) to quantify the grain size distribution, which serves as an indicator for the microstructure homogeneity. Additionally, skin depth was calculated for different frequencies of the AC and analyzed to better understand the impact of frequency on the distribution of grain sizes of FSed samples.

2 Experimental

3YSZ powder (Jiangxi Size Materials Corporation, China) and PVA (Sigma, America) were used as received. The 3YSZ powder has a particle size of 50 nm and contains trace impurities including <0.01% (in mass) SiO₂, <0.003% Fe₂O₃, <0.001% Na₂O and <0.001% TiO₂ according to the specification provided by the supplier. The powders were uniaxially pressed into dog bone-shaped specimens with a hole at the two ends, and the gage section has a length of 21 mm, a width of 3.32 mm, and a thickness of 1.90 mm. The pressed specimens were heat-treated at 600 °C for 1 h to remove PVA that was used to increase the strength of the green body.

For FS, the green body was threaded into hooks at the ends of platinum wires, and silver paste was manually

painted on both sides at the points of contact to make the Ag electrodes and reduce the contact resistance (Fig. 1). The voltage and current of specimens were monitored by a digital dynamometer (Series 730, Hioki, Japan). All the samples were flash sintered under an electrical field of about 100 V/cm, a current limit of about 1.2 A (About 190 mA/mm²) and a furnace temperature of 900 °C. DC (DSP2000-1A, Dinghua, China) and AC (108AMX-UPC12, Pacific, USA) power supplies were separately used for FS. Additionally, different frequencies (50 Hz, 500 Hz and 1 kHz) of AC were applied to samples. These samples were named DC, AC-50, AC-500, and AC-1k respectively.

In this paper, an effective AC was used and defined based on the thermal effect of the current. To determine the effective value of an AC, a resistance with the same value was used to pass both an AC and a DC. If the heat generated at the same time is equal, the value of the DC is considered the effective value of the AC.

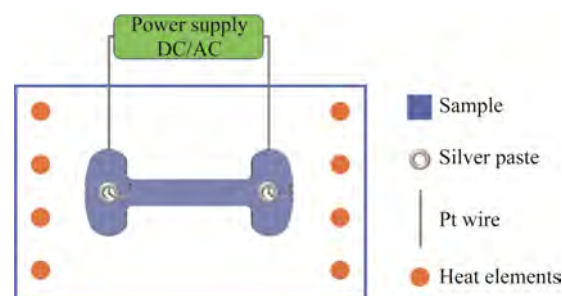


Fig. 1 Set up of FS with dog-bone samples

The microstructure evolution of different specimens was characterized by a scanning electron microscope (SEM, Mira, FEI, USA). The grain size measurements were taken at various points of the cross-section of samples and realized by the line segment method. Additionally, we follow the work by Raj^[15] in estimating the sample average temperature using the equation:

$$\frac{T}{T_0} = \left[1 + \frac{W}{\sigma A T_0^4} \right]^{-1/4} \quad (1)$$

in which T is the specimen temperature; T_0 is the temperature of the furnace; W is the power dissipation; A is the surface area of the specimen and σ is Stefan's constant. This method gives an average temperature of the specimen and is easier to execute, which is used for most of the analysis in this work.

3 Results and discussion

As shown in Fig. 2, all samples exhibited the typical FS behavior at 900 °C, *i.e.* a drop and surge in voltage and current respectively after a certain period of time, which is commonly referred to as incubation time^[16]. The important thing to note is that in all samples, the voltage before flash sintering and the maximum current were close, at approximately (200±5) V and (1.2±0.1) A, respectively. This means that the power densities are similar in all cases, which leads to similar temperatures

calculated according to Equation (1) as shown in Fig. 2(d). This makes it possible to assume that the variation

in grain size distribution is solely due to differences in AC frequency, and the effect can be studied.

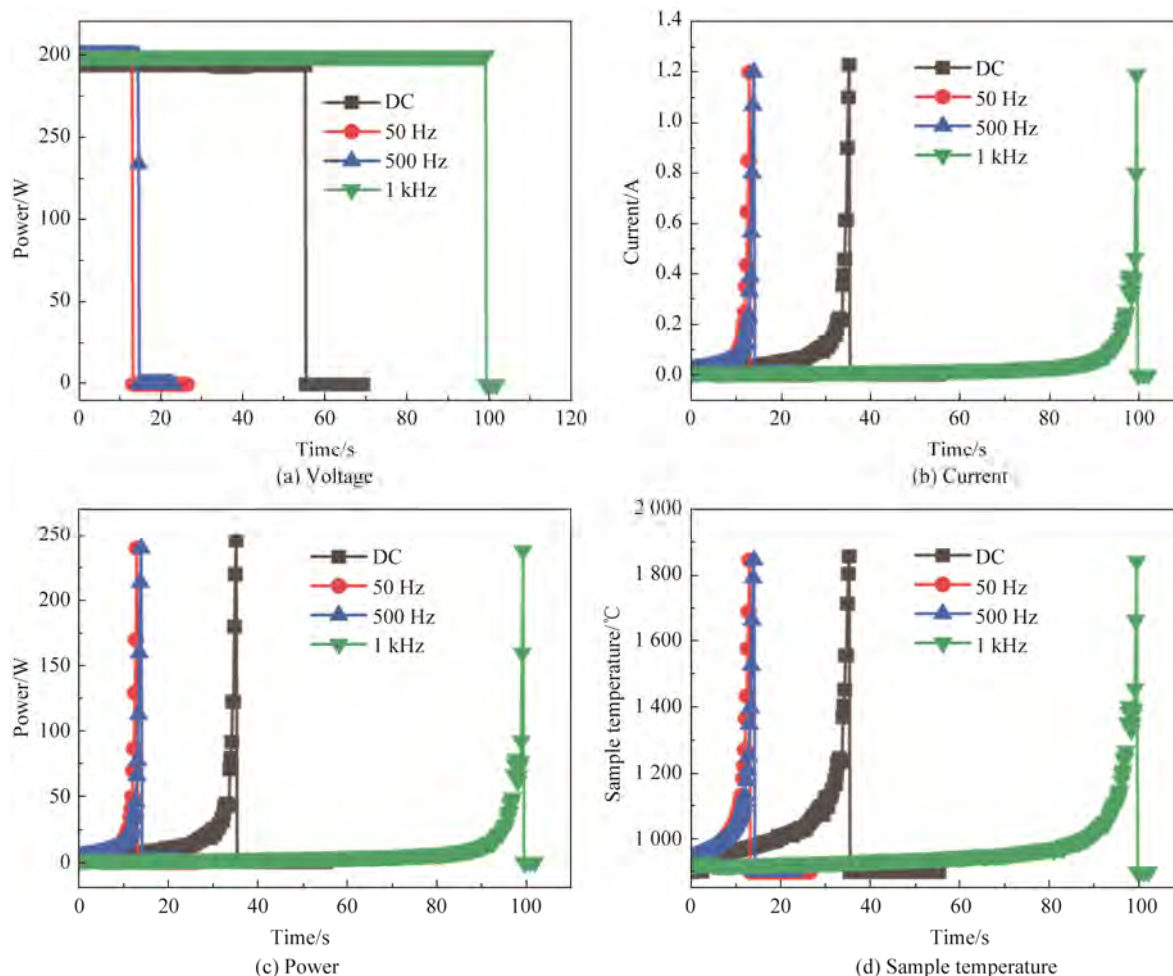


Fig. 2 Plots of the voltage, the current, the power, and the sample temperature vs. time during FS while being subjected to a power supply of either DC or AC (50 Hz, 500 Hz, and 1 kHz) at a furnace temperature 900 °C

Table 1 Width, thickness and shrinkage rate of cross-sections of FSed samples

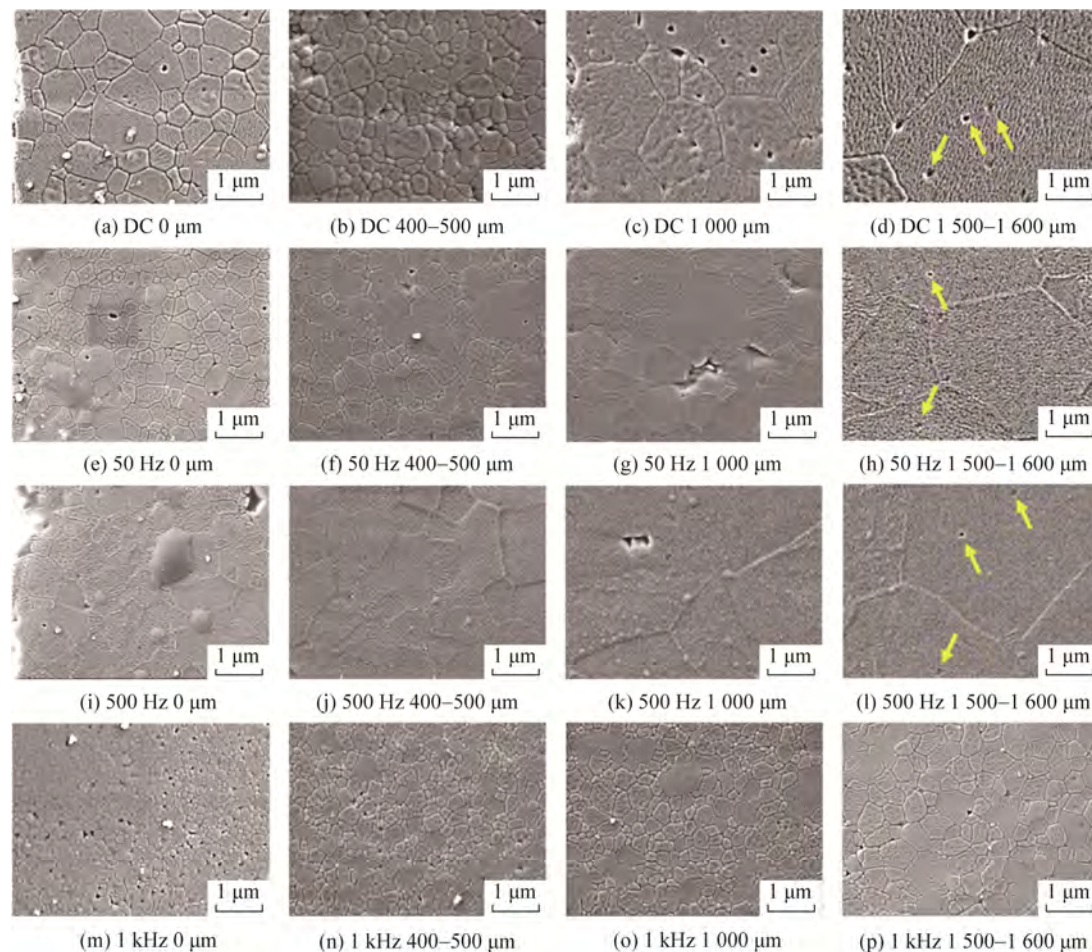
Current	Width/mm	Thickness/mm	Shrinkage rate
DC	2.64	1.40	0.20
50 Hz	2.69	1.37	0.19
500 Hz	2.69	1.40	0.19
1 000 Hz	2.66	1.41	0.20

Table 1 displays the cross-sections of various samples, which have similar areas (about 2.7 mm×1.4 mm) regardless of whether they were FSed by DC or AC. This indicates that the level of densification is similar across all samples, as they have the same size of green bodies.

The grain size was analyzed at different locations along the direction perpendicular to the current flow. The representative micrographs are shown in Fig. 3. It can be seen all samples exhibit decent levels of densification. The corresponding average grain sizes are shown in Table 2. For samples subjected to both DC and AC (50 Hz and 500 Hz), a common trend is found, which

shows increasing grain sizes from the surface to the center of the samples, similar to what is observed in DC FSed samples as reported in the literature^[11]. The ratio of the maximum to minimum grain sizes reaches to 4.9, 9.5 and 10.5 in the DC, AC-50 and AC 500 samples respectively. In Figs. 3(a)–3(c) the typical grain interior pores are observed as a result of the significant grain growth observed. Very interestingly, for sample AC-1k, the grain size from the surface to the center (about 1 600 μm from the surface) is quite similar, with the maximum to minimum grain size ratio of only 2.6. It's also worth noting that the grain size of sample AC-1k is significantly smaller than the other samples.

Fig. 4 shows the grain size variation at more locations across even larger areas, which almost range from one sample surface to the opposite one as indicated in the schematics. The results confirm that grain sizes increase as the measurement points get closer to the sample center for DC, AC-50 and AC-500, while the grain size of AC-1k is considerably smaller and much more uniform across the whole sample.



Yellow arrows indicate the intragranular pores.

Fig. 3 SEM images of grain size at different locations of the cross-sections of FSed samples along the direction perpendicular to the current flow at 0, 400–500, 1 000 and 1 500–1 600 μm from the surface while being subjected to a power supply of either (a–d) DC or AC ((e–h) 50 Hz, (i–l) 500 Hz and (m–p) 1 kHz)

Table 2 Average grain sizes of FSed samples at different locations

Distance from edge	Average grain size/ μm			
	Distance 0 μm	Distance 400–500 μm	Distance 1 000 μm	Distance 1 500–1 600 μm
DC	0.67	0.8	2.20	3.32
50 Hz	0.34	0.34	0.65	2.30
500 Hz	0.56	0.59	2.73	3.63
1 kHz	0.13	0.21	0.27	0.27

The smaller grain size at the surface might be associated with the alternating current that inhibits grain growth, which should be explored in future studies. Here, the phenomena of microstructural homogeneity are mainly discussed. In the normal FS, the heat lost through radiation and convection at the sample surface leads to a significant temperature difference between the sample's interior and surface. Therefore, the observation that the

grain size in DC flash sintering tends to decrease from the interior towards the surface of the sample is regarded to be a result of uneven temperature distribution (Fig. 5(a)) and consistent with the previous reports in the literature^[10, 17]. On the other hand, temperature gradient and uneven microstructure were also observed in lower-frequency AC flash sintering, as shown in this work and the study of Wei *et al.*^[18]. The question arises as to why only a specific frequency range can achieve the relatively homogeneous grain size distribution in AC flash sintering.

The underlying mechanism may be understood based on the “skin effect” in the AC FS process. The skin effect is the tendency of an AC to distribute within a conductor so that the current density is the largest near the surface of the conductor and decreases exponentially with greater depths in the conductor, leading to the existence of a skin depth Δ within which most of the current flows (Fig. 5(b)). The skin effect causes the current to concentrate on the surface of the sample, compensating for some of the heat loss

from radiation and convection with the external environment. As a result, the temperature inside the sample and on the surface becomes similar, which then helps to homogenize the grain size across the sample. It is noted that an optimum skin depth is expected to exist for the best effect of temperature homogenization.

The skin depth is formulated as^[19]:

$$\Delta = \sqrt{1 / \pi f \mu \gamma} \quad (2)$$

where, f , μ and γ are the frequency of AC, magnetic conductivity of samples, and electrical conductivity of samples respectively. It should be noted that Δ is inversely proportional to f , which is the only variable in the FS experiments carried out in this work. Equation (2) demonstrates that for the skin effect shown in Fig. 5(b) to be achieved, the frequency must be high enough for the skin depth to be smaller than the sample size. If the frequency is too low and the skin depth is too large, there will be no concentration of current density on the surface area. Although we could not find the magnetic conductivity value for YSZ in the literature, our experimental results indicate for YSZ samples with the size of 2–3 mm, a frequency of 1 kHz is sufficient to introduce a skin depth that can lead to a significant improvement in the microstructure homogeneity.

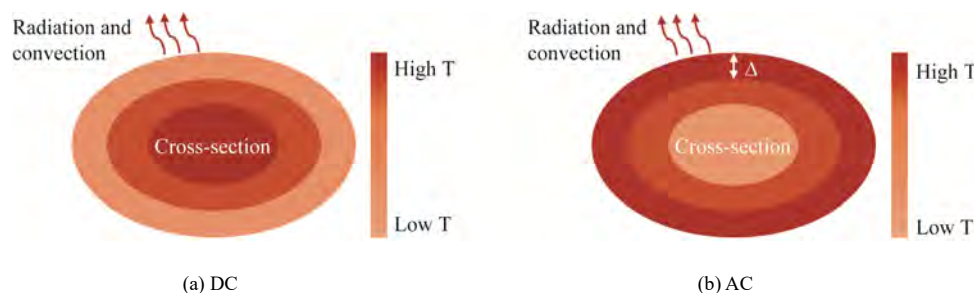
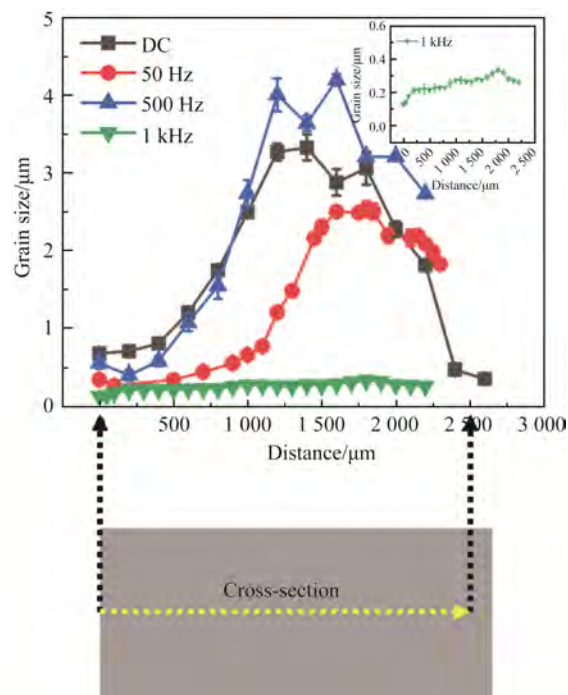


Fig. 5 Temperature distribution diagram of cross-sections of samples during FS while being subjected to a power supply of either DC or AC

4 Conclusion

The effect of AC frequency in flash sintering on the grain size distribution has been investigated. Through a comparative study of DC and AC flash sintering at varying frequencies, it has been found that a higher frequency (above 1 kHz) leads to much smaller and more uniform grain sizes.

The underlying mechanism for the more uniform grain size distribution is considered to be related to the skin effect. In the absence of the skin effect, the surface temperature is significantly lower than that inside the sample due to significant heat radiation and convection at the surface. Consequently, the internal grains of the sample are much larger than the surface grains. When the skin effect is significant, which means that the skin depth is small enough at high AC frequencies, the electric current flows predominantly on the surface of the sample.



Inset is a magnification of the sample AC-1k.

Fig. 4 Grain sizes along the direction perpendicular to the current flow while being subjected to a power supply of either DC or AC (50, 500 Hz and 1 kHz)

As a result, the temperature distribution across the cross-section of the sample becomes more uniform, leading to a more homogeneous grain size across the whole specimen.

References:

- [1] COLOGNA M, RASHKOVA B, RAJ R. Flash sintering of nanograin zirconia in <5 s at 850 °C[J]. *J Am Ceram Soc*, 2010, 93(11): 3556–3559.
- [2] XIAO W W, NI N, CHENG W L, et al. Reduced interfacial stresses in laminated ceramics during flash sintering enabled by an extremely low uniaxial viscosity[J]. *Acta Mater*, 2023, 246: 118688.
- [3] XIAO W W, NI N, FAN X H, et al. Ambient flash sintering of reduced graphene oxide/zirconia composites: Role of reduced graphene oxide[J]. *J Mater Sci Technol*, 2021, 60: 70–76.
- [4] NI N, XIAO W W, ZHENG C L, et al. Flash cosintering of a lanthanum strontium cobalt ferrite nanofibre/Gd-doped ceria bilayer structure[J]. *J Eur Ceram Soc*, 2022, 42(6): 2870–2878.

- [5] MASUDA H, MORITA K, TOKUNAGA T, et al. Anelasticity induced by AC flash processing of cubic zirconia[J]. *Acta Mater*, 2022, 227: 117704.
- [6] GHOSH S, CHOKSHI A H, LEE P, et al. A huge effect of weak dc electrical fields on grain growth in zirconia[J]. *J Am Ceram Soc*, 2009, 92(8): 1856–1859.
- [7] DOWNS J A, SGLAVO V M. Electric field assisted sintering of cubic Zirconia at 390 °C[J]. *J Am Ceram Soc*, 2013, 96(5): 1342–1344.
- [8] MCWILLIAMS B, YU J, KELLOGG F. Sintering aluminum alloy powder using direct current electric fields at room temperature in seconds[J]. *J Mater Sci*, 2018, 53(12): 9297–9304.
- [9] ALVAREZ A, DONG Yanhao, CHEN I W. DC electrical degradation of YSZ: Voltage-controlled electrical metallization of a fast ion conducting insulator[J]. *J Am Ceram Soc*, 2020, 103(5): 3178–3193.
- [10] YOSHIDA M, FALCO S, TODD R I. Measurement and modelling of electrical resistivity by four-terminal method during flash sintering of 3YSZ[J]. *J Ceram Soc Japan*, 2018, 126(7): 579–590.
- [11] LAVAGNINI I R, CAMPOS J V, JESUS L M, et al. Influence of forming methods on the microstructure of 3YSZ flash-sintered ceramics[J]. *Materialia*, 2022, 22: 101419.
- [12] BERNARDO M S, JARDIEL T, CABALLERO A C, et al. Electric current activated sintering (ECAS) of undoped and titanium-doped BiFeO₃ bulk ceramics with homogeneous microstructure[J]. *J Eur Ceram Soc*, 2019, 39(6): 2042–2049.
- [13] MISHRA T P, LENSER C, RAJ R, et al. Development of a processing map for safe flash sintering of gadolinium-doped ceria[J]. *J Am Ceram Soc*, 2021, 104(9): 4316–4328.
- [14] CARVALHO S, MUCCILLO E, MUCCILLO R. Electrical Behavior and microstructural features of electric field-assisted and conventionally sintered 3 Mol% yttria-stabilized zirconia[J]. *Ceramics*, 2018, 1(1): 3–12.
- [15] RAJ R. Joule heating during flash-sintering[J]. *J Eur Ceram Soc*, 2012, 32(10): 2293–2301.
- [16] FRANCIS J S C, RAJ R. Influence of the field and the current limit on flash sintering at isothermal furnace temperatures[J]. *J Am Ceram Soc*, 2013, 96(9): 2754–2758.
- [17] DONG Y H, CHEN I W, LI J. Transverse and longitudinal degradations in ceramic solid electrolytes[J]. *Chem Mater*, 2022, 34(13): 5749–5765.
- [18] QIN W, YUN J, THRON A M, et al. Temperature gradient and microstructure evolution in AC flash sintering of 3 mol% yttria-stabilized zirconia[J]. *Mater Manuf Process*, 2017, 32(5): 549–556.
- [19] CHUNG D D L. Pitfalls in electromagnetic skin-depth determination[J]. *J Electron Mater*, 2022, 51(5): 1893–1899.