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The impact of thermal history on the microstructure and properties of Dy-α-SiAlON

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Abstract

In order to investigate the effect of sintering schedule on the microstructure and the property, Dy-α-SiAlON ceramics were sintered by hot pressing (HP) method via three intended schedules: (1) heated the sample to 1720 °C, then rapidly cooled down to room temperature (RT), (2) heated the sample to 1720 °C, then directly cooled down to 1650 °C and hold the temperature for 60 min before cooled down to RT, and (3) heated the sample to 1720 °C and hold there for 60 min then cooled down to RT. A series of positions on the as-sintered ceramic disc along the center to the edge were chosen to study their microstructure, optical transmittance and mechanical properties. The non-uniformity of microstructure and properties along the radial direction of the as-sintered samples was justified to be caused by the varied thermal schedules. This may develop methods to fabricate gradient ceramics.

Keywords: SiAlON; Hot pressing; Microstructure; Optical properties; Mechanical properties

1. Introduction

Translucent SiAlON ceramics are a series of potential optical materials which could be used as windows or shield materials in extreme environments, through the combination of optical properties with its excellent mechanical properties, such as high hardness, wear durability, and oxidation resistance. Since translucent β-SiAlON was firstly reported by M. Mitomo[1] in 1981, lots of work on improving the transmittance of SiAlON ceramics has been conducted and has made prominent progress.[2–7] From these work we have known that SiAlON ceramics can be translucent from visible light range till 5 μm in middle infrared (MIR) region, and the maximum transmittance lies in MIR region. The reported translucent SiAlON ceramics were mainly sintered by means of hot pressing (HP) or spark plasma sintering (SPS) method: heated the sample to 1650–1900 °C and held the temperature for some time till dense ceramics were achieved, and at the same time, a 25–60 MPa axial pressure was loaded to promote the densification of the final samples.

During the HP sintering of SiAlON ceramics, liquid phase (from added oxide and oxide on the surface of Si_3N_4 and AlN) appears and then is partly absorbed or crystallized at the end of the densification process.[8] With an applied pressure, the densification process of ceramics generally experiences three stages: particle rearrangement, solution at particle contacts, and plastic flow within the solid particles.[9] The final stage is especially essential to the microstructure evolution, which is considered to accompany with the porosity elimination and grain growth.[10] As for hot pressing sintering method, the thermal energy transfers from outside into the center of the sample in the graphite die, the thermal gradient would exist during the heating and cooling process, and the different parts of the samples would experience different thermal histories, hence the evolution of microstructure and the macroscopic properties varies in some extent.

In this work, three different HP sintering schedules were designed and carried out to reveal the effect of thermal gradient on the properties and microstructure of the hot pressing sintered Dy-α-SiAlON ceramics, by fast cooling without soaking or

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Table 1
Sintering schedule of the prepared Dy-α-SiAlON ceramics.

Sample	T_1 (°C)	T_2 (°C)	Soaking time at T_2 (min)
S1	1720	1720	0
S2	1720	1650	60
S3	1720	1720	60

soaking at a certain temperature. The research showed an effective way to control the impact of thermal gradient and offered a possible way to fabricate ceramics with gradient microstructure and gradient properties as well.

2. Experimental

The starting powders were α-Si_3N_4 (E10 grade, UBE Industries Ltd., Tokyo, Japan), AlN (grade A. Starck, Berlin, Germany) and Dy_2O_3 (99.99%, Yuelong Nonferrous Metals Co., Ltd., Shanghai, China). The composition point of this work was $m=2$, $n=1$ according to the formula $M_{m/v}$–$Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$, and the electrovalent balancing cation (M^{v+}) of α-SiAlON phase is Dy^{3+}.

The mixtures of the starting powders were ball milled in Si_3N_4 jar with Si_3N_4 balls for 20 h. Ethanol was used as milling medium. Then the homogenized slurry was dried and followed by passing through an 80 mesh sieve to obtain an agglomerate-free powder mixture. Sintering process was carried out in a graphitic furnace. The mixed powders were directly pressed in the graphitic die and sintered following three different schedules: (1) heated the samples to 1720 °C ($T_1=T_2$), then cooled down to room temperature (RT) without soaking, (2) heated the samples to 1720 °C (T_1), then rapidly cooled down to 1650 °C (T_2) and held the temperature for 60 min before cooled down to RT; and (3) heated the samples to 1720 °C and held there for 60 min ($T_1=T_2$) then cooled down to RT. The three schedules are also listed and illustrated in Table 1 and Fig. 1a. The sintered samples were named as S1, S2 and S3 respectively according to the sintering schedule. Then the as-sintered samples were sliced and polished into thin plates, and five points on the sample along the center to the edge were selected for the subsequent analysis (Fig. 1b).

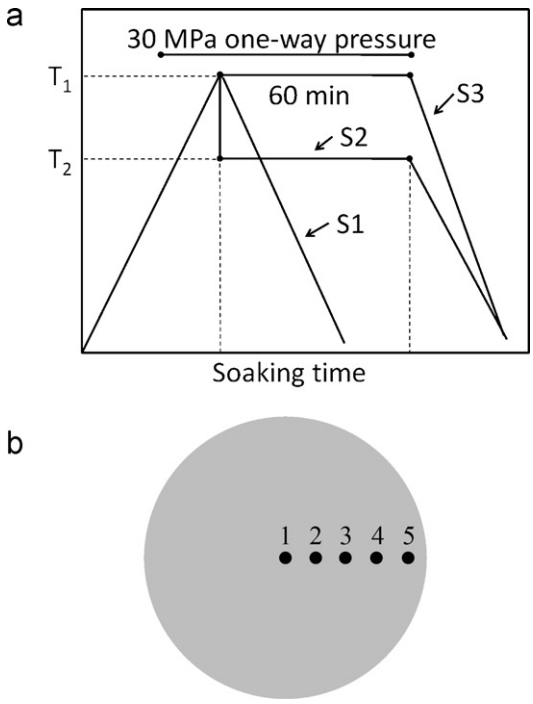

Fig. 1. Sketch map of (a) sintering schedule of the samples and (b) selected five points on the sintered Dy-α-SiAlON samples along the radial direction.

Table 2
Bulk density and mechanical properties of the as-sintered Dy-α-SiAlON samples.

Sample	Bulk density (g/cm^3)	Positions	Vickers hardness (GPa)	Fracture toughness (MPa m$^{1/2}$)
S1	3.28	1	11.4	2.92
		2	11.8	3.05
		3	11.9	3.06
		4	13.1	3.12
		5	15.8	3.20
		Ave.[a]	12.9 ± 1.7	3.1 ± 0.2
S2	3.62	1	18.6	3.13
		2	18.5	3.12
		3	19.0	3.25
		4	19.2	3.28
		5	19.7	3.27
		Ave.[a]	19.0 ± 0.6	3.2 ± 0.2
S3	3.63	1	18.4	3.89
		2	18.5	3.91
		3	19.0	3.92
		4	18.7	3.80
		5	19.0	3.90
		Ave.[a]	18.7 ± 0.4	3.9 ± 0.2

[a] The average value of the five positions from the center to the edge on the disc samples.

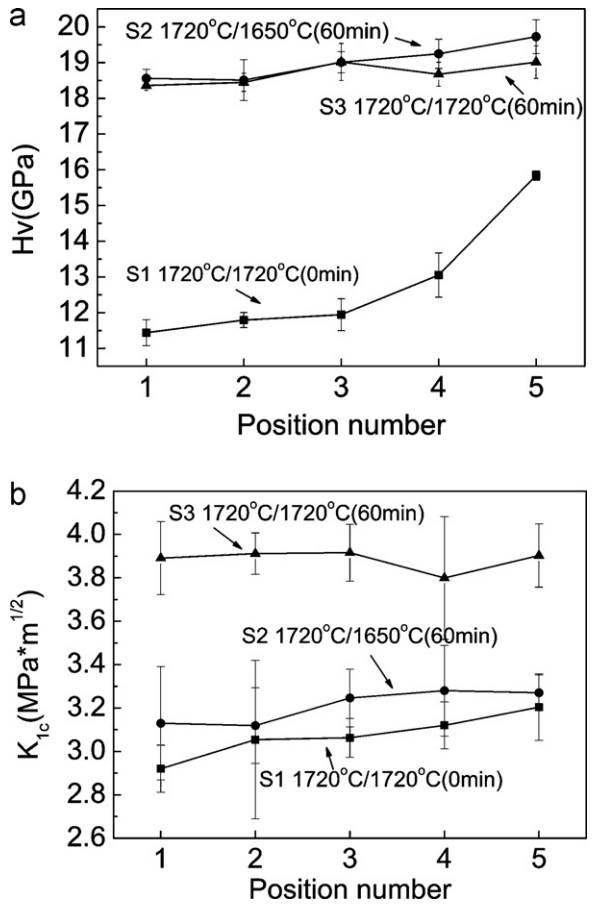

Fig. 2. (a) The Vickers hardness and (b) the indentation fracture toughness of sample S1, S2 and S3. Positions 1–5 represent the five positions from the center to the edge of the three samples, respectively.

The density of the sintered ceramics was measured by the Archimedes principle. The Vickers hardness as well as indentation fracture toughness were determined at room temperature using Vickers diamond indenter with a load of 10 kg for 10 s and calculated according to the method of Evans.[11] The samples were sliced and polished to 0.8 mm in thickness with the surface perpendicular to the HP direction for optical transmittance measurement (FTIR; EQUINOX55, Bruker, Billerica, MA). The backscattered electron images were obtained under an electron probe microanalysis (EPMA; 8705QH2, JEOL, Tokyo, Japan). Field-emissive scanning electronic microscope (FE-SEM; JSE-6700F, JEOL, Tokyo, Japan) was used to observe the fracture surface of the specimens, and the average grain size was calculated according to the SEM images.

3. Results and discussion

The bulk density values of the as-sintered samples S1–S3 are listed in Table 2, where an obvious change in density can be found for the three samples experienced different thermal schedules. The bulk density of sample S1 without soaking is quite low, 3.28 g/cm^3. The density value of sample S2 is 3.62 g/cm^3, while sample S3 possesses a slightly higher density value than that of S2, is 3.63 g/cm^3, which achieves a full density (this will be further demonstrated by microstructure observation). The increase of density reflects a truth that soaking process is much essential to the densification of Dy-α-SiAlON, either for sample S2 holding at 1650 °C (60 min) or for sample S3 holding at 1720 °C (60 min).

Then five positions on each sample S1, S2 and S3 were specified for the mechanical and optical property measurements and also for microstructure analysis. Vickers hardness (Hv) and indentation fracture toughness (K_{1c}) were chosen to represent the mechanical performance of the samples, and the optical transmittance was measured in middle infrared region.

The Hv and K_{1c} values of the three samples are listed in Table 2. The Vickers hardness values of the five positions on sample S1 increase from the center (11.4 GPa) to the edge (15.8 GPa) of the disc. As for the sample S2 and S3, after soaking at 1650 °C and 1720 °C for 60 min, their Hv values reach up higher than 18 GPa, much higher than the value of sample S1 from the center to the edge on the surface. Similarly, the Hv values of samples S2 and S3 also show a tendency of increasing, but the extent of increasing is much lower than that of sample S1. Obviously, a soaking schedule can greatly increase the Hv values, as for the situation of samples S2 and S3, a relatively uniform Hv value distribution is achieved on the ceramic discs (the standard Hv deviation is only ±0.6 and ±0.4 for S2 and S3, respectively, seen in Table 2). During the heating/cooling process, the thermal energy transfers from the outside into the center of sample, and a thermal gradient along the radial direction formed inside the specimens due to its low thermal conductivity, accompanied with a microstructure change in the sample. So the effect from the thermal gradient is the main reason for the increase of Hv on sample S1, along the radial direction from point 1 to point 5. As for the lower Hv value of point 1 in sample S1, it can also be deduced from the cross section image of the sample where there are plenty of pores in sample S1 (Fig. 3a(1)). This kind of microstructure must be easily deformed under a high pressure applied in the mechanical measurement. The porosity decreasing from the center to the edge reflects on the increase of Hv along a negative direction. Comparatively, the samples S2 and S3 are nearly pore-free and the grains in the two samples are all well-packed (Fig. 3b and c), which are the most important factors for the high Hv value of samples S2 and S3.

The variation of fracture toughness in samples S1–S3 is quite different from that of Hv. The standard deviation values of K_{1c} are much lower than the ones of Vickers hardness (Table 2), that means that there is no obvious gradient of K_{1c} in the three samples from the center to the edge on the surface. Compared with sample S1, the K_{1c} of sample S3 is improved markedly due to undergoing a soaking procedure at 1720 °C for 60 min. But for sample S2, soaked at a lower temperature (1650 °C) for 60 min, its K_{1c} value is not significantly improved (Fig. 2b). These results are also supported by microstructure analysis. It is generally believed that the SiAlON ceramics with elongated grains possess higher K_{1c} values than those with equiaxed grains.[12] It can be seen in Fig. 3 that there are plenty of equiaxed grains in samples S1 and S2, and intergranular fracture mainly happens on the cross sections (Fig. 3a, b). While for the sample S3, the elongated grains can be easily found and both intergranular fracture and

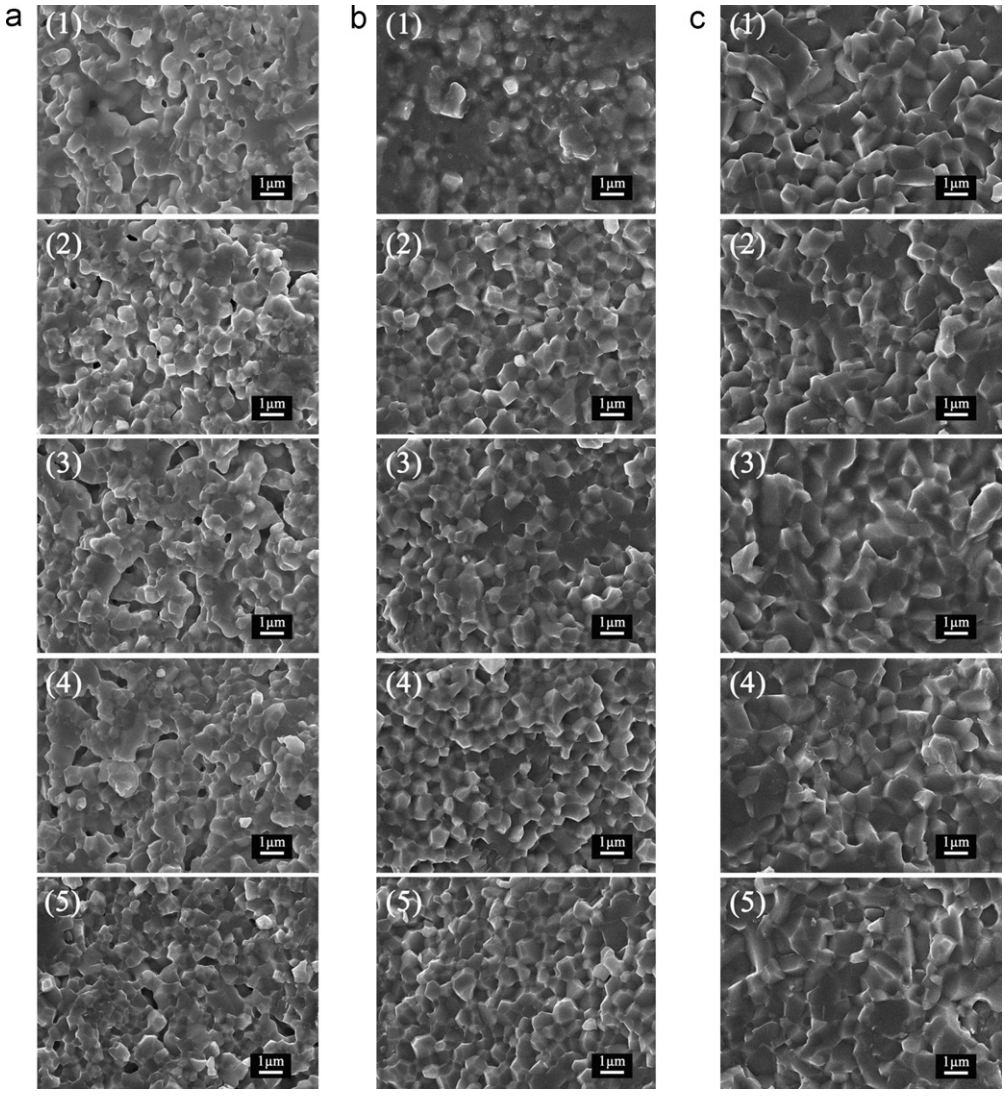

Fig. 3. Cross section morphology of the as-sintered SiAlON ceramic samples (a) S1, (b) S2 and (c) S3. The figures 1–5 in (a), (b) and (c) represent the five positions along the center to the edge of S1, S2 and S3, respectively.

transcrystalline rupture happened on the cross sections (Fig. 3c). It is the mixed fracture mechanism that improves the K_{1c} value of sample S3.

Observing with naked eyes, in visible light range, sample S1 is opaque, sample S2 is translucent except the central area (position S2-1 and S2-2), and sample S3 is translucent in all area. The transmittance (T) curves of samples S2 and S3 are shown in Fig. 4. It is also opaque at the center of sample S2 in middle infrared region. There is a bit light transmittance at position S2-2 at 4.5 μm wavelength, while the other three positions close to the edge of sample S2 are highly translucent and possess a similar light transmittance value of 52% (Fig. 4a). In the SEM images of the polished surface of sample S2 (Fig. 5), it is clear that there are lots of pores on the surface at the two positions near the center (S2-1 and S2-2), which indicates that the residual pores are the major light scattering source that significantly reduces the transmittance at positions S2-1 and S2-2. The variety in porosity of sample S2 is caused by the heat transfer gradient during HP process. At first, the front-end of thermal energy reaches the edge of the ceramic, so the edge part firstly achieves the required sintering conditions (i.e. adequate liquid phase and proper liquid viscosity) for pore elimination. With the thermal gradient moving forward, the pore-free area expands from the edge to the center. As for our experiment, this process did not finish in the center area of sample S2 due to the lack of driving force for sintering at lower temperature of 1650 °C. Of course, the non-uniformity of density is also partly resulted from the non-uniformity of the axial pressure. But for sample S3, after soaked at 1720 °C, the pore elimination process fully finished and the sample was translucent in middle infrared region. It is worth to notice that the light transmittance of sample S3 is lower than the value of S2 and further decreases from the center to the edge, with at most 6% T loss (Fig. 4b).

To discuss the loss of the transmittance of sample S3, a microstructure analysis is necessary. It can be seen that the grain size of sample S3 increases from the center to the edge (Fig. 6), which is also caused by the thermal gradient during the sintering process. So the light transmittance loss of sample S3

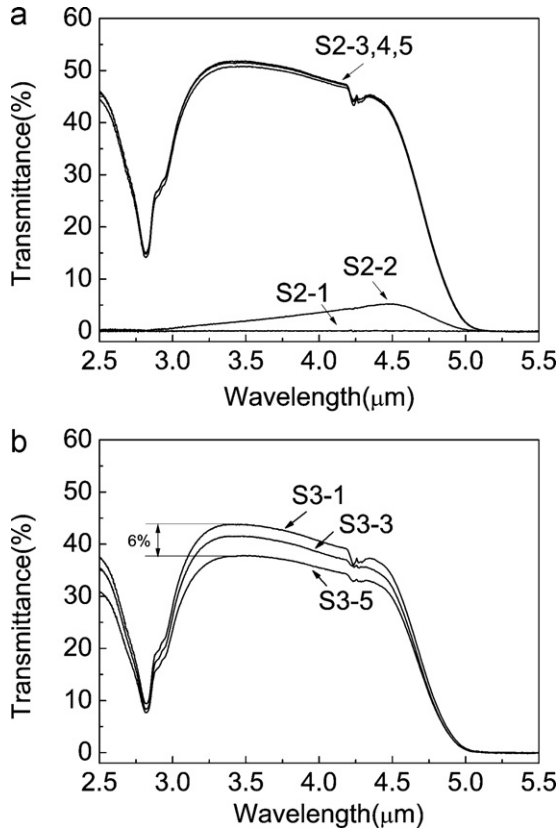

Fig. 4. The transmittance curve of sample (a) S2 and (b) S3 in infrared region. Lines S2-1–S2-5 represent the five positions from the center to the edge of sample S2, respectively, and the same correspondence is performed for the sample S3 (0.8 mm in thickness).

has a close relationship with the non-uniformity of grains. The abnormal grain growth in sample S3 might cause much more light-scattering that reduces its transmittance. For sample S2, its average grain size is slightly larger than that of sample S1, but much smaller than S3 (Fig. 6), and also its grains are uniform along the radial direction. The observation implies that the grain growth process in sample S2 was restrained (almost the same average grain size with S1) while the densification process was

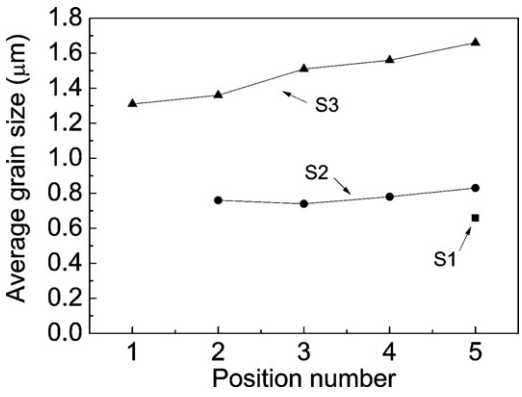

Fig. 6. Average grain size of samples S1, S2 and S3. The figures 1–5 represent the five positions along the center to the edge of S1, S2 and S3, respectively. There is no obvious grain outline in the SEM image of positions 1–4 on S1 and position 1 on S2, hence the grain size was not measured. However, it can be deduced that the average grain size of position 5 on S1 is the largest in sample S1.

sustained (same density with S3) when soaking at 1650 °C. In other words, the abnormal grain growth of Dy-α-SiAlON can be inhibited to some extent by soaking at a lower temperature, therefore the transmittance is increased.

4. Conclusion

During hot pressing sintering, the heat transfer gradient can result in a slight change in grain morphology and gradient pore dispersion along the center to the edge of the Dy-α-SiAlON disc samples, which makes the macroscopic properties including Hv, K_{1c}, and transmittance, vary accordingly. The thermal gradient during the fast heating or cooling process resulted in a significant non-uniformity of microstructure and Hv values of sample S1 along the center to the edge. But the non-uniformity could be restricted and the Hv values could be improved by soaking samples at higher temperature (1720 °C) or lower temperature (1650 °C) for 60 min. In infrared region, the light transmittance of sample S3 soaked at 1720 °C for 60 min, decrease along the center to the edge on the disc sample due to the abnormal grain growth. The abnormal grain growth could be restricted

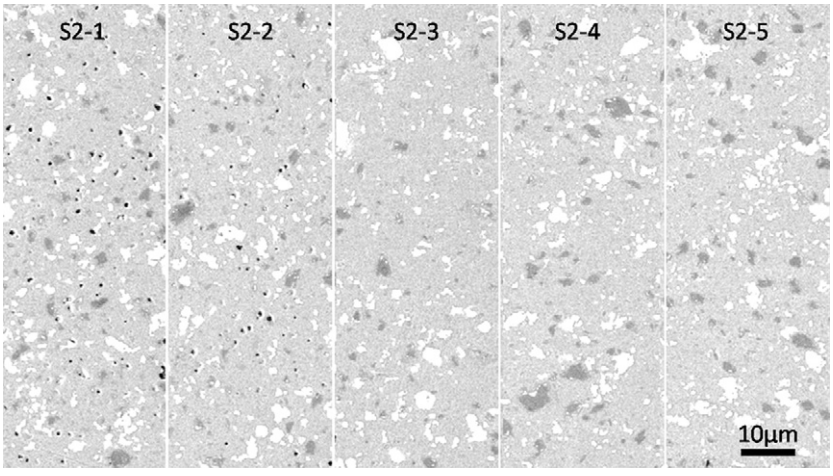

Fig. 5. SEM images of the polished surface of sample S2. Series S2-1–S2-5 represent the five positions on sample S2 from the center to the edge, respectively.

by soaking sample at a lower temperature (1650 °C for 60 min) and then a higher transmittance of sample S2 was achieved. However, the proper sintering schedule to fabricate highly uniform α-SiAlON ceramics, either in morphology or in properties, needs some further detailed investigation.

From a different angle, the thermal gradient can be enlarged if intendedly lowering the thermal conductivity of the samples or increasing the heating or cooling rate. And this strategy might be one of the effective methods to fabricate gradient functional materials with gradient change of properties and microstructure along the radial direction.

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