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Effect of LiYO_2 on the synthesis and pressureless sintering of Y_2SiO_5

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Y_2SiO_5 has potential applications as a high-temperature structural ceramic and environmental/thermal barrier coating. In this work, we synthesized single-phase Y_2SiO_5 powders utilizing a solid-liquid reaction method with LiYO_2 as an additive. The reaction path of the $\text{Y}_2\text{O}_3/\text{SiO}_2/\text{LiYO}_2$ mixture with variation in temperatures and the role of the LiYO_2 additive on preparation process were investigated in detail. The powders obtained by this method have good sinterability. Through a pressureless sintering process, almost fully dense Y_2SiO_5 bulk material was achieved with a very high density of 99.7% theoretical.

I. INTRODUCTION

Yttrium silicate (Y_2SiO_5) is an important laser crystal that has been synthesized since 1963.¹ Most research activities are related to rare-earth (Ce^{3+} , Eu^{3+} , etc.)-doped Y_2SiO_5 crystals to be used as blue phosphor or Cr^{4+} -doped Y_2SiO_5 as a saturable absorber Q-switch laser.²⁻⁴ Although spectroscopic studies of doped Y_2SiO_5 have been widely performed, the fundamental properties of the host crystal itself are still lacking.

Y_2SiO_5 is also recognized as a precipitated phase at the grain boundaries of sintered Si_3N_4 with Y_2O_3 or $\text{Y}_2\text{O}_3+\text{SiO}_2$ sintering aids, and it is an important phase in the $\text{SiO}_2\text{-Y}_2\text{O}_3\text{-Si}_3\text{N}_4$ phase diagram.^{5,6} The melting point of Y_2SiO_5 is 1950 °C, which renders it a potential high-temperature structural material.⁷ Y_2SiO_5 has good chemical stability, and its thermal expansion coefficient ($8.36 \times 10^{-6}/\text{K}$ for polycrystalline sample) matches well with that of most non-oxide ceramics. For instance, a high-performance $\text{SiC}/\text{Y}_2\text{SiO}_5$ multilayer coating with good erosion resistance and low residual stress at the interface was developed recently.⁸ Moreover, the low evaporation rate of Y_2SiO_5 along with its low oxygen permeability constant at temperatures up to 1900 °C endows this material with excellent oxidation resistance.⁹ Y_2SiO_5 coatings can efficiently improve the high-temperature performance of silicon-based ceramics.^{9,10}

Unfortunately, preparation of single-phase Y_2SiO_5 is very difficult because a strict stoichiometric ratio of the starting $\text{Y}_2\text{O}_3/\text{SiO}_2$ is needed.⁷ At present, the sol-gel process and powder-mixing route have been used for the synthesis of Y_2SiO_5 powders.¹⁰⁻¹² In the sol-gel method, precursors of $\text{Y}(\text{NO}_3)_3$ and TEOS (tetraethyl orthosilicate) are put in ethanol to form a $\text{Y}_2\text{O}_3/\text{SiO}_2$ gel, and then Y_2SiO_5 powders can be synthesized by calcining the gel above 900 °C. Because the stoichiometric ratio of the two precursors can be accurately controlled, pure Y_2SiO_5 can be obtained via this method. However, this method is not suitable for volume production. In addition, the precursors are very expensive. Another method for Y_2SiO_5 preparation is to calcine $\text{Y}_2\text{O}_3\text{-SiO}_2$ powders directly by a solid-state reaction.^{10,12} This method is convenient for preparation of ceramic powders and has been widely used in the ceramic industry. The shortcoming of this method is the difficulty in controlling the proportioning of starting materials and the slow reaction rate. Thus Y_2SiO_5 powders always contain a mass of impurities. Furthermore, for solid-state reaction synthesis of Y_2SiO_5 , a high calcination temperature (>1600 °C) and long holding time (>15 h) are needed.¹²

Due to the difficulties in the preparation of Y_2SiO_5 , the sintering and properties of bulk Y_2SiO_5 material have not yet been reported. The fundamental mechanical properties, including elastic moduli, hardness, strength as well as the thermal properties of this polycrystalline material, are not yet available.

In this paper, we report a solid-liquid reaction method to synthesize single-phase Y_2SiO_5 at a relatively low

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temperature (1500 °C) with a short dwell time (2 h) by introducing a LiYO₂ additive. LiYO₂ has been used in sintering of Si₃N₄ as a new type of effective, single-component additive.¹³ It significantly lowered the sintering temperature of silicon nitride due to the presence of LiO₂ in the SiO₂-Y₂O₃ system, which led to formation of a low-viscosity liquid phase.¹⁴ In the present work, LiYO₂ was used as an additive to accelerate the reaction velocity between yttria and silica. Addition of LiYO₂ dramatically lowered the synthesis temperature, shortened the dwell time, and eliminated the undesirable phases. In addition, the Y₂SiO₅ powders synthesized by this method have good sinterability, and the fully dense bulk material can be obtained by pressureless sintering of the powders at 1500 °C for 1 h. The effects of the LiYO₂ additive on the synthesis process were investigated.

II. EXPERIMENTAL

Y₂O₃ and amorphous SiO₂ powders were ball-milled in isopropyl alcohol with 0, 1, and 3 mol% LiYO₂ additive for 10 h. The powder mixture was then calcined at 1500 °C for 2 h in air and ball-milled again for 24 h to break up agglomerates. The formed Y₂SiO₅ powders were subsequently screened through a 150-mesh sieve. To understand the role of LiYO₂ additive in the synthesis of yttrium silicate, the reaction heat flow of Y₂O₃/SiO₂ and Y₂O₃/SiO₂/LiYO₂ powder mixtures during calcining to 1450 °C at a rate of 2 °C/min was monitored using a differential scanning calorimeter (DSC, Setaram Setsys 16/18, Caluire, France). Based on the DSC results, some Y₂O₃/SiO₂/LiYO₂ samples were calcined to different temperatures and were analyzed by x-ray diffraction (XRD) to examine the phase formation during the heating process. The content of LiYO₂ additive in the Y₂O₃/SiO₂/LiYO₂ powders for both DSC test and the subsequent sintering is 3 mol%.

Green-body compaction was formed by uniaxially pressing the powders into pellets at 40 MPa and then isostatically cold pressing them at 260 MPa. The density of green body approached ≈60% of the theoretical value (the theoretical density is 4.44 g/cm³). Shrinkage behavior was monitored using a thermal mechanical analyzer (TMA, Setaram Setsys 24) by heating the sample up to 1500 °C in air at a rate of 5 °C/min. A series of compacts were sintered at different temperatures in the range of 1350–1500 °C for 60 min. Fully dense Y₂SiO₅ was ultimately obtained after sintering at 1500 °C for 1 h in air.

The synthesized Y₂SiO₅ powders were characterized by XRD (Rigaku D/max-2400, Rigaku, Tokyo, Japan). The theoretical XRD pattern of Y₂SiO₅ was simulated using the diffraction package in the Cerius² computational program for material science (Molecular Simulation, Inc., San Diego, CA). The microstructure of the

etched surface was observed by a SUPRIA 35 scanning electron microscope (SEM, LEO, Oberkochen, Germany).

III. RESULTS

XRD patterns of the synthesized powders calcined at 1500 °C for 2 h with different amounts of LiYO₂ additive are illustrated in Fig. 1. When the additive was free [Fig. 1(a)], the reaction products were very complicated. A large amount of yttria was detected, in addition to small amounts of γ -Y₂Si₂O₇, Y₂SiO₅, and Y-apatite, Y_{4.67}(SiO₄)₃O. This result demonstrated that the reaction between yttria and silica was very insufficient. With 1 mol% LiYO₂ additive [Fig. 1(b)], the content of Y₂O₃ decreased but that of Y_{4.67}(SiO₄)₃O apatite increased notably. In this case, the portion of Y₂SiO₅ was still small. When the content of the additive was increased to 3 mol%, the XRD pattern [Fig. 1(c)] shows that the product is single-phase Y₂SiO₅, and the experimental result is in good agreement with the simulated pattern [Fig. 1(d)]. Obviously, with the addition of LiYO₂ additive, the reaction between SiO₂ and Y₂O₃ was accelerated significantly.

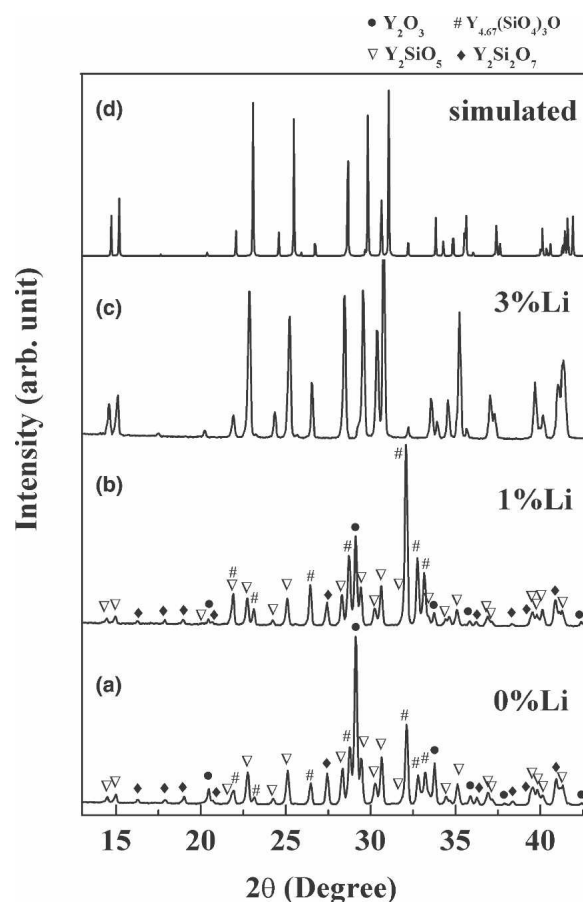


FIG. 1. (a–c) XRD patterns of Y₂SiO₅ powders synthesized at 1500 °C for 2 h in air with different amounts of LiYO₂ additive; (d) simulated pattern using Cerius² computational software.

The influence of LiYO_2 additive on the synthesis of Y_2SiO_5 can also be determined from DSC thermographs and XRD spectra collected from the powders after DSC testing (Fig. 2). The thermograph of the Y_2O_3 and SiO_2 powder mixture without LiYO_2 additive had a broad exothermal peak in the range of 600–1450 °C [Fig. 2(a), $\text{Y}_2\text{O}_3/\text{SiO}_2$]. In combination with XRD analysis [Fig. 2(b)], the broad exothermal peak corresponded to the crystallizations of silica. But for the sample with added LiYO_2 [Fig. 2(a), $\text{SiO}_2/\text{Y}_2\text{O}_3/\text{LiYO}_2$], three sharp exothermal peaks appeared at 834, 960, and between 987 and 1023 °C, along with an endothermic peak at 980 °C. The corresponding XRD result showed that, after DSC test, LiYO_2 -containing powders were crystalline Y_2SiO_5 and $\text{Y}_{4.67}(\text{SiO}_4)_3\text{O}$ with a small trace of Y_2O_3 and amorphous silica. To better understand the phase evolution during the heating process, parallel runs were conducted in the temperature range of 600–1500 °C where reactions might occur, i.e., compacts of the $\text{SiO}_2/\text{Y}_2\text{O}_3/\text{LiYO}_2$ powders were heated up to a desired temperature at 10 °C/min, held there for 10 min, and then cooled down to room temperature. These samples were examined by XRD for phase identification, and the results are summarized in Table I. Based on the XRD results, the exothermic peak at 834 °C corresponded to the formation of $\text{Y}_{4.67}(\text{SiO}_4)_3\text{O}$, while the sharp exothermic peak at 960 °C should originate from the presence of $\text{X1-Y}_2\text{SiO}_5$ (a low-temperature polymorph of Y_2SiO_5 , which can transform to high-temperature polymorph Y_2SiO_5 at ≈ 850 – 1100 °C; the reported transition temperatures vary^{10,11,15}). The only endothermic peak at 980 °C was derived from the liquid-phase formation, and the broad exothermic peak between 987 and 1025 °C corresponded to the formation of large amounts of $\text{Y}_{4.67}(\text{SiO}_4)_3\text{O}$ and Y_2SiO_5 .

The pressureless sintering behavior of Y_2SiO_5 was studied by TMA. As presented in Fig. 3(a), the relative density ρ/ρ_0 and the densification rate $(1/\rho)d\rho/dt$ are plotted as a function of sintering temperature up to 1500 °C at 5 °C/min in air. We found that the Y_2SiO_5 compact started to shrink at 1050 °C, and the fastest shrinkage took place at 1200 °C. When the final temperature of 1500 °C was reached, the relative density of Y_2SiO_5 was up to 98.7% of theoretical. To optimize the sintering procedure, isothermal densification experiments were conducted at the temperature range of 1350–1500 °C [Fig. 3(b)]. The results in Fig. 3(b) show that the Y_2SiO_5 powders prepared by this method have good sinterability. When heated at 1350 °C for 1 h, the relative density of compacts was higher than 95%. After a 1-h hold at 1500 °C, nearly 100% relative density was achieved. Figure 4 presents the microstructure of Y_2SiO_5 sintered at 1500 °C for 1 h. The sample was fully dense with an appearance of equiaxed grains. The grain size was ≈ 6 μm on average (see Fig. 4).

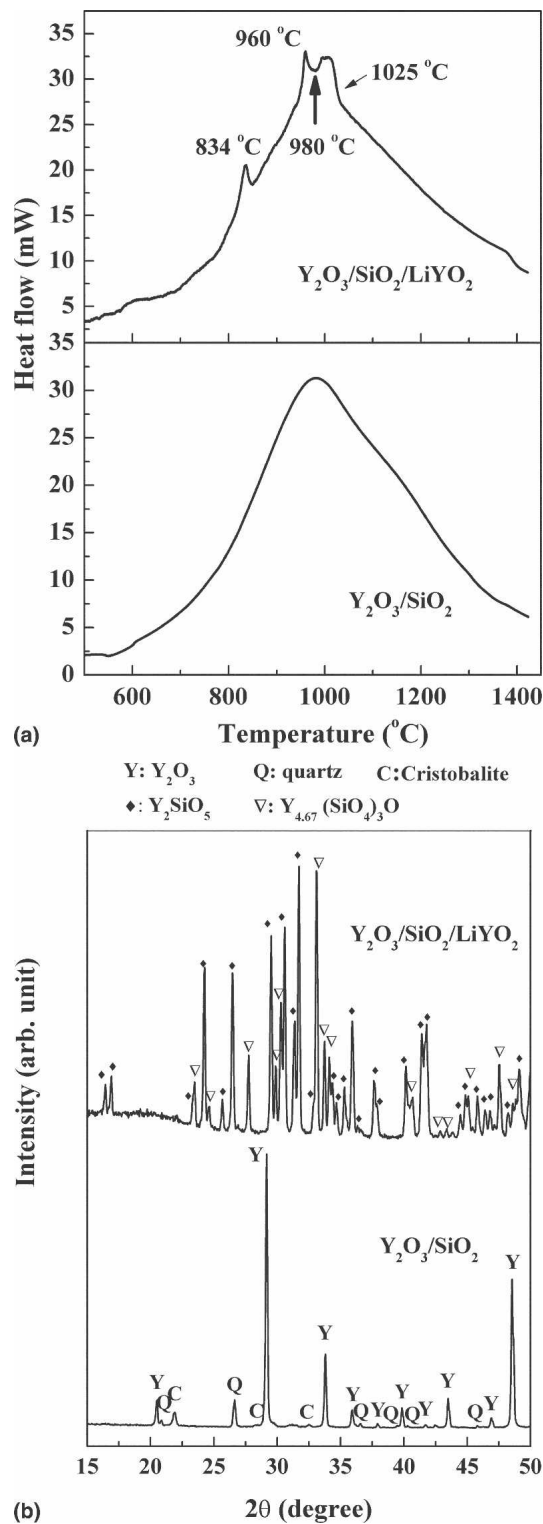


FIG. 2. (a) DSC thermographs of $\text{Y}_2\text{O}_3/\text{SiO}_2$ and $\text{Y}_2\text{O}_3/\text{SiO}_2/\text{LiYO}_2$ powder mixtures heated to 1450 °C at a rate of 2 °C/min; (b) corresponding XRD pattern after DSC test.

IV. DISCUSSION

In this paper, we successfully obtained single-phase Y_2SiO_5 powders utilizing a novel solid-liquid reaction

TABLE I. The phases identified in Y₂O₃/SiO₂/LiYO₂ powder mixture heated to different temperature regions.

Temperature (°C)	Phases identification
Below 830	Y ₂ O ₃ , amorphous SiO ₂ , quartz
830–840	Y ₂ O ₃ , amorphous SiO ₂ , quartz, Y _{4.67} (SiO ₄) ₃ O ^a
840–980	Y ₂ O ₃ , amorphous SiO ₂ , quartz, Y _{4.67} (SiO ₄) ₃ O ^a , X1-Y ₂ SiO ₅ ^{a,b} , Y ₂ Si ₂ O ₇ ^a
980–1025	Y _{4.67} (SiO ₄) ₃ O, Y ₂ O ₃ , Y ₂ SiO ₅ , γ-Y ₂ Si ₂ O ₇ ^a
1025–1450	Y ₂ SiO ₅ , Y _{4.67} (SiO ₄) ₃ O, Y ₂ O ₃
1500 and holding	Y ₂ SiO ₅

^aA small trace.

^bX1-Y₂SiO₅ is the low-temperature polymorph of Y₂SiO₅, which can transform to X2-Y₂SiO₅ (high-temperature polymorph, here written as Y₂SiO₅ for brevity).

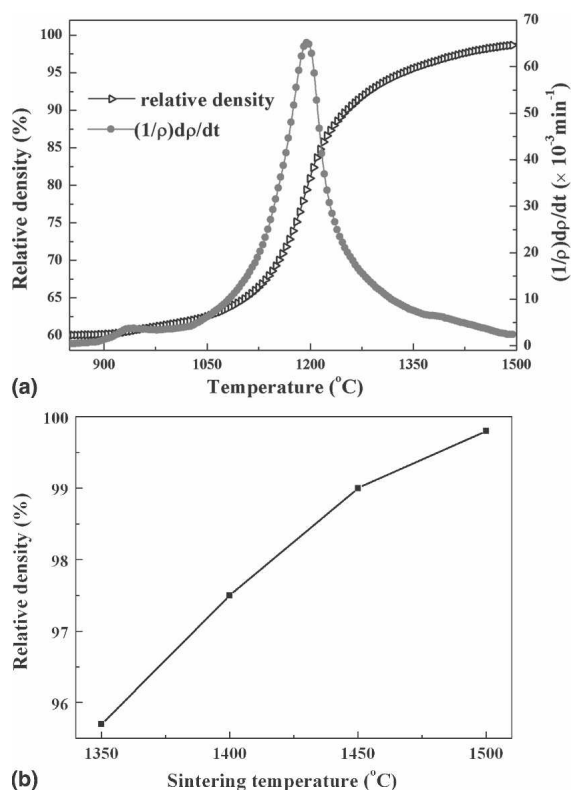


FIG. 3. (a) Relative density and densification rate plotted as functions of temperature during heating at 5 °C/min to 1500 °C; (b) final densities of the samples sintered at different temperatures for 1 h.

method with LiYO₂ additive. From Figs. 1 and 2 we see that LiYO₂ plays a key role in the synthesis of Y₂SiO₅. As reported in previous work by Kim et al., at 1225 °C, LiYO₂ and SiO₂ could form a liquid phase,¹⁶ which would act as a “molten pool” and allow for rapid transportation of various substances. The DSC results [Fig. 2(a)] show liquid-phase formation at 980 °C, which was slightly lower than that reported in Ref. 16. This liquid phase was aroused by LiYO₂ and should be a Li–Si–Y–O phase. The important point was that this liquid phase facilitated a complete reaction between Y₂O₃

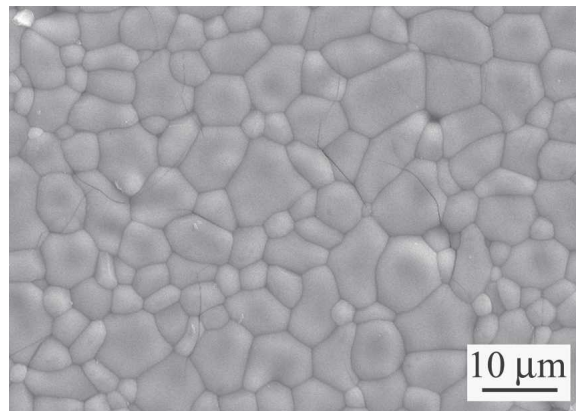
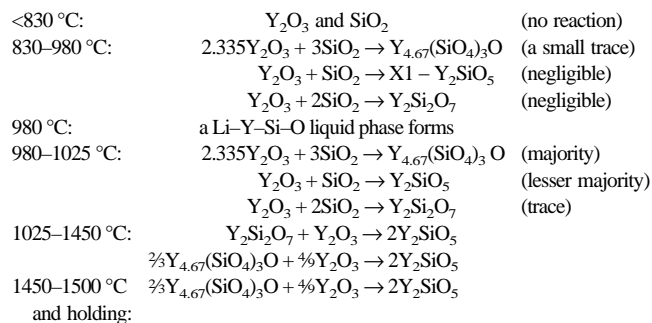


FIG. 4. Microstructure of the etched surface of Y₂SiO₅ after sintering at 1500 °C for 1 h in air.

and SiO₂ at a low temperature range with a short duration. Based on analysis of DSC and XRD results, we could hypothesize the possible reactions occurred during the heating process. When no additive was added, except for the crystallization of silica, only small amounts of Y_{4.67}(SiO₄)₃O, γ-Y₂Si₂O₇, and Y₂SiO₅ were found, and the reaction between silica and yttria could be ignored [Fig. 1(a)]. In addition, the comparatively higher peaks in accordance with Y_{4.67}(SiO₄)₃O, indicated that formation of Y_{4.67}(SiO₄)₃O was superior to that of others. With addition of LiYO₂, based on the temperature dependence of DSC and XRD phase analysis using the powders heated to different temperatures as listed in Table I, the reaction paths could be speculated as follows:



These reaction paths revealed that Y_{4.67}(SiO₄)₃O had a lower formation energy than Y₂SiO₅ and Y₂Si₂O₇, and it turned out to be the major product below 1025 °C. When the temperature was lower than 980 °C, the reaction between Y₂O₃ and SiO₂ was negligible. Above 980 °C, due to the liquid-phase formation, Y₂O₃ and SiO₂ reacted rapidly, and Y_{4.67}(SiO₄)₃O and Y₂SiO₅ became predominant. Above 1025 °C, Y_{4.67}(SiO₄)₃O would react with residual Y₂O₃ to form Y₂SiO₅ step-by-step.

The influence of LiYO₂ additive in the synthesis process of Y₂SiO₅ was proved to be significant in our experiment. LiYO₂ as an additive was chosen for several

reasons. First, based on the Li₂O–Y₂O₃–SiO₂ ternary-phase diagram,¹⁷ the presence of lithian compound could lower the reaction temperature of Y₂O₃–SiO₂ by a eutectic reaction. Second, with introduction of LiYO₂, a Li–Si–Y–O liquid phase developed at 980 °C, favoring reaction between Y₂O₃–SiO₂. Third, LiYO₂ can decompose into Li₂O and Y₂O₃ at ≈1400 °C, and Li₂O would evaporate rapidly due to its high evaporation pressure.¹⁸ Matovic et al.¹³ measured the evaporation rate of LiYO₂ during sintering of Si₃N₄ with LiYO₂ additive. They observed that the Li₂O content in specimens decreased from 15 to 0.08 wt% after they were held at 1500 °C for 8 h. Therefore, we could also prolong the dwell time for powder preparation to evaporate Li ions sufficiently and consequently to eliminate the influence of residual Li ions on the high-temperature performance of Y₂SiO₅.

V. CONCLUSIONS

(1) Pure single-phase Y₂SiO₅ powders were prepared by calcining Y₂O₃ and SiO₂ powder mixtures at 1500 °C for 2 h with 3 mol% LiYO₂ additive. After pressureless sintering of the as-synthesized powders at 1500 °C for 1 h in air, fully dense Y₂SiO₅ bulk ceramic was obtained.

(2) LiYO₂ additive played a key role in the synthesis of Y₂SiO₅ due to the liquid-phase formation at 980 °C, which acted as a “melting pool” and favored the rapid transportation of various substances through it. The Li–Y–Si–O liquid phase aroused by the LiYO₂ additive lowered the synthesis temperature, shortened the reaction time, and provided the synthesized powder a good sinterability.

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