The effect of microstructure control on mechanical properties of 12Ce-TZP via two-step sintering method

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Abstract

The nanopowders of 12Ce-TZP were synthesized by a solid state reaction method and the effect of two-step sintering (TSS) on the microstructures and mechanical properties of the ceramics were studied. The samples obtained by conventional sintering (CS) exhibit approximately 2.5 μm in grain size and only 6.99 GPa in Vickers hardness, as well as 425 MPa in bending strength. To control the microstructure and consequently optimize the mechanical properties, different TSS regimes were conducted. The results indicate that first firing at 1450 °C for 1 min followed by cooling down to 1300 °C with a soaking time of 30 h results in a highly densified (98.4% TD) ceramic with optimal mechanical properties (9.22 ± 0.26 GPa, 14.7 ± 0.66 MPa·m^{1/2}, 501.40 ± 16.21 MPa) and without significant grain growth (~ 1 μm). This provides an economic and effective approach to controlling the microstructure and thereby improving the mechanical properties of 12Ce-TZP ceramics.

Keywords: 12Ce-TZP ceramics; Two-step sintering; Microstructure; Mechanical properties

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1. Introduction

Tetragonal zirconia polycrystals (TZP) have been paid wide attentions for a long period because of their high strength and excellent fracture toughness [1]. Typically 3Y-TZP, which exhibits both high strength (800-1500 MPa) and high hardness ($\sigma_f > 10$ GPa), has been extensively used in the abrasive and biomedical fields [2]. However, due to moderate fracture toughness ($4\text{--}5 \text{ MPa}\cdot\text{m}^{1/2}$) and poor resistance to low temperature degradation (LTD), the further application of 3Y-TZP in different industries is limited [3,4]. Compared to 3Y-TZP, 12Ce-TZP possesses high toughness ($10\text{--}15 \text{ MPa}\cdot\text{m}^{1/2}$) and excellent durability to hydrothermal degradation (aging) [5]. Nevertheless, 12Ce-TZP has not been generally used as a structure ceramic, due to its very low hardness (~ 7 GPa) and limited strength (300-500MPa).

It is well known that the properties of polycrystalline ceramics are in close correlation with the microstructure. For instance, 12Ce-TZP exhibiting lower hardness and strength as compared to 3Y-TZP is possibly due to its larger grains. Hence, extensive studies have been conducted to suppress the grain growth of 12Ce-TZP to improve its mechanical properties [6-8]. Generally, two principal ways are applied to achieve this goal: doping with other oxides to result in grain boundary strengthening and changing the sintering process to control grain size. Numerous researches have reported that the strength of ceramics can be markedly increased by means of finely distributed second phases, which will pin grain boundaries [9-11]. Composites such as alumina, titanates, spinel tend to segregate at the grain boundary which can prohibit the grain growth of 12Ce-TZP, resulting in higher strength or toughness [12-14]. However, Chakravarty reported that with increasing of MgO doping content above a certain level, densification of sub-micro Al_2O_3 was retarded, which exhibited a negative effect on the mechanical properties of the ceramics [15]. Moreover, it is not easy to achieve a well distribution of fine second phase in ceramics to inhibit grain growth. Thus, seeking for other ways to control grain size becomes quite meaningful. Another common way to suppress grain growth is adoption of different sintering methods. It is well established that cerium oxide can accelerate grain growth, which is also considered to always accompany final-stage sintering in conventional sintering process, resulting in coarse grain size of 12Ce-TZP. While grain boundary migration and grain boundary diffusion are two key factors for grain growth, the former contributes primarily to grain growth and the latter mainly contributes to densification. Hence, if the temperature is set at a certain range where grain boundary diffusion is active, but grain boundary migration is restrained, densification will continue without any significant grain growth. Various methods such as hot pressing, spark plasma sintering (SPS) and pulsed electric current sintering (PECS), have been attempted to prepare kinds of ceramics [16-19]. These methods have generated such benefits as a rapid sintering rate, high densification, fine grain size distribution [20]. It is, however, hardly accessible and rarely used for practical applications which may be because these methods are not cost-effective due to complex and expensive devices [21].

Chen and Wang have proposed a new approach called two-step sintering (TSS) for Y_2O_3 fabrication [22], which suppresses grain growth by adjusting the correlation between grain boundary diffusion and grain boundary migration. The key factors in this method include firstly heating up to a higher temperature T_1 to conduct first-step sintering with a shorter soaking time, then lowering the temperature to T_2 followed by a longer soaking time to conduct second-step sintering during which only densification occurs without significant grain growth [23]. In addition to Y_2O_3 , TSS has been widely applied to Al_2O_3 [24], ZnO [25], BaTiO_3 [26], as well as the fabrication of $\text{Gd}_2\text{Zr}_2\text{O}_7$ [27]. However, little attention has been devoted to two-step sintering of 12Ce-TZP.

In this work, TSS was carried out in the fabrication of 12Ce-TZP to achieve the microstructure refinement. Since T1 and T2 play a completely different role in the sintering mechanism of TSS process respectively, the effects of temperature of both sintering steps on densification and grain size were studied by designing different TSS regimes. Furthermore, the effect of microstructure evolution on the mechanical properties of 12Ce-TZP ceramics was investigated.

2. Experimental procedure

2.1. Sample preparation

12Ce-TZP powders were prepared by a conventional solid state reaction method. The raw materials used were CeO₂ (Rare-Chem Hi-Tech Co., Ltd., AR Grade, purity $\geq 99.99\%$) with a particle size of about 400 nm and ZrO₂ (Decheng Chemical Co., Ltd., AR Grade, purity $\geq 99.99\%$) with a particle size of about 500 nm, which were firstly preheat-treated at 800 °C for 3h with the aim of removing any absorbed water. Then, the stoichiometric mixed powders were ball-milled in ethanol using high-purity YSZ balls for 24 h and then high-energy ball-milled at 2500 r·min⁻¹ for 3 h, followed by drying at 70 °C for 12 h to evaporate the ethanol. The dried mixtures were ground and sieved to obtain the final powders with a particle size of approximately 80 nm and a specific surface area of 30 m²/g. The powders were uniaxially die-pressed under 20 MPa, followed by cold isostatic pressing under 200 MPa into green pellets. The pellets were sintered by conventional sintering (CS) and two-step sintering (TSS) methods. CS was conducted at 1400 °C to 1500 °C with 50 °C intervals and a heating rate of 0.05°C/s (see Table 1). For the first step of TSS, the samples were heated to the same temperature with conventional sintering with a heating rate of 0.08°C/s and a dwell time of 1 min to ascertain the appropriate T1 (see Table 2). For the second step, 1200 °C to 1300 °C with a holding time of 30 h under the same T1 and a cooling rate of 0.8°C/s between T1 and T2 was selected to confirm the appropriate T2 (see Table 4), so as to achieve a high densification.

2.2. Characterization

The phase structure of all sintered samples were examined by X-ray diffraction (XRD, Bruker, D8 Advance) with Cu K α radiation. The lattice parameters were determined by a slow scanning over the range 20-80° with the rate of 0.02° s⁻¹. The microstructure of the fracture surfaces of samples was examined by field emission scanning electron microscopy (FSEM, Zeiss, Sigma 500) with an image analyzer to measure the mean grain sizes of both CS and TSS samples. The bulk density of the sintered compacts was measured by Archimedes method with deionized water as immersion medium, while 6.25 g/cm³ was used as the theoretical density for all the samples, calculated from the lattice parameters and the molecular weight contained in per unit cell. The average grain size of all sintered samples was determined on representative SEM micrographs according to the linear intercept method with an Image-pro software by counting more than 200 grains per specimen. The shrinkage data was calculated by comparing the diameters of sintered and pressed green compacts.

2.3. Mechanical properties measurement

For indentation and fracture toughness test, the samples were ground by SiC paper with different meshes and polished by diamond pastes to produce mirror-like surfaces. Prior to tests, the samples were annealed to eliminate the residual stress generated during grinding and polishing. Then the Vickers hardness tests were carried out on a Vickers hardness tester (Hengyi, EM-4500) with an indentation load of 1 kg and a dwell time of 15 s, while an indentation load of 50 kg was used for the fracture toughness tests. The distance between indentations was kept for a certain value in order to avoid any overlapping effect [28]. As soon as the indentation process had been completed, the lengths of the two diagonals and cracks were measured by an optical microscopy. The fracture

toughness was calculated according to the equation proposed by Niihara [29], using an elastic modulus of 190 GPa, a general value for 12Ce-TZP ceramics. At least five indentations were made for each sample and the results were averaged in order to obtain systematically accurate values. The three-point bending strength was measured on 5 bar samples (50 mm × 3 mm × 4 mm) using a universal tester (Chuangyuan, WDW3200) with a crosshead speed of 0.5 mm/min. Bending strength (σ) was calculated according to the following relation:

$$\sigma = \frac{3PL}{2bh^2}$$

where P, L, b and h represent the maximum load of sample damage (N), the length of the support span (mm), width (mm) and height (mm), respectively.

3. Results

3.1. Conventional sintering

The XRD patterns of the samples prepared under different sintering temperature for 3 h are shown in Fig. 1. The sample sintered at 1450 °C is composed of a pure tetragonal structure. While the specimens sintered under 1400 °C and 1500 °C are consisted of the tetragonal and monoclinic phases, indicated by the presence of XRD peaks at 2θ values of about 28° and 31°.

The microstructures of fracture surfaces of all conventionally sintered samples are presented in Fig. 2. As can be obviously seen, all of the compacts have dense polygonal matrixes and distinct grain boundaries in the grain size of about several micrometers, which can be attributed to ceria promoting sintering process and accelerating the grain growth. Fig. 3 shows the relationship between the relative density and grain size of all samples as a function of sintering temperature under different CS conditions. When the sintering temperature is below 1400 °C, no significant grain growth is detected while the densification proceeds constantly as the temperature increases. At the higher temperature, however, the grain growth is accelerated ranging from 1.08 to 3.25 μm but the fractional density just slightly increased from 97.2% to 98.6% TD (theoretical density).

The shrinkage ratio and mechanical properties of all specimens prepared under different sintering temperature are summarised in Table 1. The shrinkage ratio of the sample sintered under 1400 °C is the highest (22.16%). The hardness and fracture toughness exhibits entirely opposite tendency as a function of sintering temperature. With the increase of temperature, the hardness of all samples decreases from 7.74 to 6.47 GPa in relation to the concomitant dramatic grain growth. Meanwhile, the fracture toughness slightly increases from 13.9 to 15.2 $\text{MPa}\cdot\text{m}^{1/2}$.

3.2. Two-step sintering

Since conventional sintering method usually leads to remarkable grain growth of 12Ce-TZP, two-step sintering is applied to achieve the goal of inhibiting the grain growth and obtaining finer grain sizes. Owing to the T1 and T2 making a distinct difference in the sintering procedure, different sintering regimes are designed to study the effect of temperature of two stages on the densification and grain growth of 12Ce-TZP ceramics, respectively.

Since relevant sintering technology about 12Ce-TZP ceramics have been rarely reported before, different TSS regimes are introduced with fixed T2 (see Table 2) to highlight the effect of first-stage temperature referring to the TSS process of 3Y-TZP and the CS procedure of 12Ce-TZP ceramics. Except for TSS2 specifically marked with a heating rate of 10°C/min to make a comparison with TSS3 under the same temperature to examine the influence of heating rate, the rest regimes are designed with the same heating rate of 5°C/min to study the effect of T1 on the densification and grain growth.

Fig. 4 shows the XRD patterns of the compacts prepared under different TSS conditions (T2 fixed). As can be clearly seen, the results correlate well with that of the CS condition. Similarly,

single tetragonal structure is obtained only when T1 is 1450 °C, as evidenced by the standard XRD spectra of t-ZrO₂.

Fig. 5 presents the SEM micrographs of all compacts sintered under different TSS conditions. It can be observed that compared with the samples sintered under CS regimes, the microstructure refinement is obtained with more homogenous and finer grains in the size of nanometers. However, the samples seem not so dense as that of CS conditions, as indicated in Table 3. Table 3 summarizes the shrinkage ratio, relative density, grain size and mechanical properties of all compacts sintered under different TSS conditions (T1 fixed). The shrinkage ratio of all samples are lower than that of CS. Although the grain growth is retarded and the final grain sizes are far smaller than that of CS, a higher densification can not be obtained without remarkable grain growth. Moreover, the sample sintered at 1400 °C (T1) possesses the highest hardness of 9.55 GPa, which is improved to a large extent compared with that of CS due to microstructure refinement in spite of a relatively lower density. Overall, the hardness decreases linearly with the increase of T1 and the fracture toughness increases gradually from 11.8 to 13.5 MPa·m^{1/2} at the same time, mainly associated with the coarser microstructure.

Since the holding time at T2 (30h) is fairly long, T2 (1150 °C) is probably too low for densification in the process. Consequently, three different TSS regimes are designed with temperature interval of 50 °C (see Table 4) to study the effect of T2 on the microstructural evolution. The XRD patterns of all samples sintered under different TSS conditions are exhibited in Fig. 6. Evidently, all of the ceramics are composed of pure tetragonal structure, which are consistent with the superstructure peaks of t-ZrO₂. Fig. 7 shows the SEM micrographs of all samples sintered under different TSS conditions (T1 fixed). It can be clearly seen that all ceramics possess polygonal grains with dense microstructures and the grain boundaries are clean, which are in agreement with the results summarized in Table 5. The shrinkage ratio, relative density, grain size and mechanical properties of all compacts sintered under different TSS regimes (T1 fixed) are listed in Table 5. The sample sintered under TSS7 possesses the highest shrinkage ratio (21.95%). In contrast to TSS2 and TSS3 cycles (T2 fixed), enhanced densification with slightly coarsened grain size is obtained. Although the grain size varies from 824 nm to 1 μm, the relative density increases from 96.5% to 98.4% TD, which is almost equal to that of CS condition (98.6% TD). Moreover, the fracture toughness of the samples increases from 14.0 to 14.7 MPa·m^{1/2} with the increase of T2, while the hardness slightly decreases from 9.46 to 9.22 GPa, mainly attributed to the concomitant grain growth with the variation of T2.

4. Discussion

4.1. Conventional sintering

As for the specimen sintered under 1400 °C for 3 h, the temperature may be not sufficient to form single tetragonal phase since the sintering of 12Ce-TZP needs a high temperature due to its intrinsic properties. As to the specimen sintered under 1500 °C, the appearance of monoclinic phases is probably due to the higher temperature resulting in a coarser microstructure, in correlation with the SEM micrograph (Fig. 2c), which exceeds the critical grain size for spontaneous transformation. The shrinkage ratio of all samples slightly decreases with increasing temperature, which is associated with the coarser microstructure. Hence, 1450 °C is the appropriate temperature in the CS process for preparing 12Ce-TZP ceramics.

In conventional sintering, increasing of relative density is always accompanied by significant grain growth. Since higher temperature providing higher activation energy for both grain boundary diffusion and grain boundary migration according to sintering kinetics. Therein, the densification process during CS is mainly ascribed to the grain boundary migration, which also contributes to

rapid grain growth. Consequently, it is a key factor to ascertain the sintering temperature in the CS method of 12Ce-TZP ceramics to suppress the grain boundary migration to prohibit the grain growth.

It is well established that the microstructure is the basis of the properties, in turn, the properties reflect the microstructure at the same time. As described before, the main deficiency of 12Ce-TZP is low fracture strength and low hardness, which is largely due to its large grains. Therefore, despite the slightly improved fracture toughness which can be attributed to the enhanced transformability caused by grain growth, the strength and hardness are still too low to meet the demand of practical applications.

4.2. Two-step sintering

It has been reported that T1 has a crucial influence on the critical density and second-stage sintering [22]. Only achieving a high critical relative density in the first stage to render the pores open and unstable, stimulating the triple-point (junction) drag mechanism [23], the grain boundary movement will be inhibited as a result. Thus, the influence of T1 is firstly studied. In view of the phase composition, coupled with the hardness and fracture toughness, 1450°C is the optimum temperature regardless of CS or TSS (T1) methods. In addition, the influence of heating rate is also examined by comparing TSS2 with TSS3. It is apparent that both densification and grain size are lower when faster heating is applied, whereas the microstructure refinement is not obvious and the densification is sacrificed at the same time. Hence, common heating rate of 5°C/min is appropriate in the TSS regimes. As appeared in Table 3, the densification rises with the increase of T1, while all samples are not fully dense. Due to insufficient densification and relatively high porosity, the shrinkage ratio of all samples are lower than that of CS. In fact, T1 is high enough for the samples to achieve desired critical relative density for that of CS. Moreover, the dwell time at T2 (30h) is adequately long for the grain boundaries to mobile to conduct the densification process. Therefore, it is necessary to further investigate T2 to achieve both high density and small grain size.

As explained previously, a high densification can not be obtained although the microstructure is refined largely, which is probably due to the low T2 insufficient for proceeding the densification process. It is generally accepted that after the critical density is achieved to make the pores open and unstable in the first-stage sintering, the dispersed open pores can pin grain boundaries and retard grain boundary migration in the second-stage sintering, for which the grain growth is suppressed [30]. However, if T2 is too low, the grain boundary diffusion which usually leads to densification will be restrained, if too high, the grain boundary migration will be activated which usually results in dramatic grain growth. Thus, an appropriate T2 is considerably important for the densification and suppression of grain growth in the TSS method.

As can be seen in Table 5, the higher T2, the denser microstructure obtained, resulting in the highest shrinkage ratio of the sample sintered under T2 of 1300 °C. Because of T2 providing activation energy for grain boundary migration and grain boundary diffusion, while for the latter, the energy level demand is lower. Therefore, with the increase of T2, the grain boundary diffusion is firstly activated and proceeds, promoting the densification process and thereby achieving a higher density [31]. Hence, the density reaches a maximum level when T2 is 1300 °C. Since with the variation of T2, the decrease of hardness is so small that can be ignored, coupled with the high fracture toughness and high density when T2 is 1300°C, thus, the optimum T2 for the fabrication of 12Ce-TZP ceramics is 1300 °C. In addition, as indicated in Table 1 and Table 5, the bending strength of the sample prepared under TSS7 condition is higher than that sintered under 1450 °C for 3 h, which is attributed to the synergism of refined microstructure and high relative density.

Fig. 8 illustrates a comparison made of the grain growth evolution versus relative density of

12Ce-TZP ceramics between CS and TSS methods. It can be clearly seen that in the conventional sintering method, the later stage of densification process is always accompanied by remarkable grain growth. However, in the two-step sintering, densification process proceeds without significant grain growth. For instance, for the samples prepared under T1 of 1450 °C and T2 of 1300 °C, higher densification is achieved without grain growth with increasing holding time ranging from 10h to 30h compared with that sintered under CS method which possesses a similar grain size.

As is well known, the key to two-step sintering method (TSS) is the determination of T1 and T2, which are equally important in the process. Although the grain growth is mainly inhibited in the second-step sintering under T2, the temperature of the first-step sintering (T1) has a significant influence on the initial grain size and critical density, which are in tight correlation with the triple-point drag mechanism [22]. Once T1 is sufficiently enough to obtain an appropriate critical density to make the pores unstable, it is possible for the ceramics to achieve high densification without significant grain growth, related to the dispersed open pores as mobile particles on the grain boundaries which can retard grain growth [32]. In the second-step sintering, it is significant to adjust the correlation between grain boundary migration and grain boundary diffusion. For grain boundary migration mainly contributes to the grain growth and the grain boundary diffusion is conducive to the densification process, in order to achieve high densification without detectable grain growth the grain boundary diffusion needs to keep active, while the grain boundary migration ought to be suppressed. Thus, an appropriate T2 is both important for prohibiting the grain boundary migration to retard the grain growth (not too high) and conducting the grain boundary diffusion to promote the densification process (not too low). In our work, T1 and T2 are well modulated to adjust the sintering kinetics to obtain 12Ce-TZP ceramics with high density and fine grain size distribution. Meanwhile, the mechanical properties of the ceramics are greatly improved through the microstructure refinement.

4. Conclusions

The effects of different TSS conditions on the densification and grain growth, as well as the mechanical properties of 12Ce-TZP ceramics are investigated and compared with that of CS conditions to study the influence of microstructure control on the mechanical properties of 12Ce-TZP ceramics. The results can be summarized as follows:

1. High density 12Ce-TZP ceramics with a grain size of several micrometers can be obtained through conventional sintering under 1450 °C for 3 h. Nevertheless, due to the large grain size, the hardness and strength of the sample are fairly low (6.99 ± 0.31 GPa, 425.19 ± 14.76 MPa).
2. To attain the microstructure refinement and improve the mechanical properties, different two-step sintering regimes are applied. It is indicated that 12Ce-TZP nanoceramics with a grain size of 690 nm can be obtained by firstly heating up to 1450 °C, followed by cooling down to 1150 °C with a holding time of 30 h. Although the hardness has been greatly improved to 8.98 ± 0.22 GPa, the relative density is just moderate (95.8% TD) and the fracture toughness is sacrificed (13.1 ± 0.55 MPa·m^{1/2}).
3. Taking advantage of the discrepancy between the grain boundary migration and grain boundary diffusion, the TSS regimes are further modified to achieve high density without remarkable grain growth as well as optimized mechanical properties. It is shown that high density (98.4% TD) 12Ce-TZP ceramics with a grain size of approximately 1 μm can be obtained by firing at 1450 °C for 1 min followed by holding at 1300 °C for 30 h. The hardness, fracture toughness and strength of the sample prepared under the optimum TSS condition are 9.22 ± 0.26 GPa, 14.7 ± 0.66 MPa·m^{1/2} and 501.40 ± 16.21 MPa, respectively.

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Table 1

Mechanical properties of all samples prepared under different sintering temperature

Temperature (°C)	Holding time (h)	Shrinkage (%)	Vickers hardness (GPa)	Fracture toughness (MPa·m ^{1/2})	Bending strength (MPa)
1400	3	22.16	7.74 ± 0.38	13.9 ± 0.44	425.19 ± 14.76
1450	3	21.61	6.99 ± 0.31	14.8 ± 0.46	
1500	3	21.11	6.47 ± 0.26	15.2 ± 0.54	

Table 2
Summary of two-step sintering conditions (T_2 fixed)

Conditions	T_1 ($^{\circ}\text{C}$)	t_1 (min)	T_2 ($^{\circ}\text{C}$)	t_2 (h)
TSS1	1400	1	1150	30
TSS2	1450 (10 $^{\circ}\text{C}/\text{min}$)	1	1150	30
TSS3	1450	1	1150	30
TSS4	1500	1	1150	30

Table 3

Relative density, grain size and mechanical properties of 12Ce-TZP compacts sintered under different TSS conditions (T2 fixed)

Conditions	Shrinkage (%)	Relative density (%)	Grain size (nm)	Vickers hardness (GPa)	Fracture toughness (MPa·m ^{1/2})
TSS1	20.98	93.92 ± 0.12	416.42 ± 13.50	9.55 ± 0.38	11.8 ± 0.38
TSS2	21.23	95.36 ± 0.16	564.09 ± 17.60	9.26 ± 0.29	12.3 ± 0.49
TSS3	21.49	95.84 ± 0.19	690.10 ± 19.80	8.98 ± 0.22	13.1 ± 0.55
TSS4	21.74	96.80 ± 0.20	860.20 ± 22.20	8.54 ± 0.17	13.5 ± 0.57

Table 4
Summary of two-step sintering regimes (T_1 fixed)

Regimes	T_1 (°C)	t_1 (min)	T_2 (°C)	t_2 (h)
TSS5	1450	1	1200	30
TSS6	1450	1	1250	30
TSS7	1450	1	1300	30

Table 5

Relative density, grain size and mechanical properties of 12Ce-TZP compacts sintered under different TSS conditions (T1 fixed)

Conditions	Shrinkage (%)	Relative density (%)	Grain size (nm)	Vickers hardness (GPa)	Fracture toughness ($\text{MPa}\cdot\text{m}^{1/2}$)	Bending strength (MPa)
TSS5	21.61	96.48 ± 0.18	824.62 ± 41.15	9.46 ± 0.41	14.0 ± 0.32	
TSS6	21.70	97.60 ± 0.15	918.28 ± 45.32	9.30 ± 0.33	14.3 ± 0.45	
TSS7	21.95	98.40 ± 0.12	1030.41 ± 48.55	9.22 ± 0.26	14.7 ± 0.66	501.40 ± 16.21

Figure 1

Figure

Figure

(b)

Figure

(c)

Figure 3

Figure 4

Figure

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Figure 6

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Figure 8