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## PREPARATION OF FINE GRAINED SiC AT REDUCED TEMPERATURE BY TWO-STEP SINTERING

### WYTWARZANIE DROBNOZIARNISTEGO SiC W OBNIŻONEJ TEMPERATURZE PRZEZ DWUETAPOWE SPIEKANIE

Two-step sintering route was applied for the densification SiC by promoting the role of liquid phase. The specimen contained 8 vol% of liquid phase composed of Al<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub>. The heating schedule consisted with initial rapid heating to 2000°C and immediate quenching to 1700 or 1750°C. By heating at elevated temperature, even distribution of the liquid phase was intended. The heat treatment at reduced temperature was to suppress the evaporative loss of the liquid and to secure the time for densification. The two-step sintering effectively suppressed loss of mass and coarsening. The resultant SiC was thus dense and was composed of fine grains exhibiting hardness of 2321 kgf/mm<sup>2</sup>.

*Keywords:* SiC, Liquid phase, Two-step sintering, Coarsening, Hardness

## 1. Introduction

Owing to excellent mechanical properties and chemical stability, SiC is essentially used for materials at harsh environment such as armors and aerospace [1]. Dense SiC is necessary to obtain the mechanical properties and is generally prepared by sintering at elevated temperature under external pressure to overcome the nonsinterable nature of the covalent bonded material.

An alternative route of densification is a liquid phase sintering, which admits the rapid transport of material through wet boundary at reduced temperature. As the liquid phase sintering can be carried out without a pressure device such as hot press, it can be applied to the production of complex shaped product at a reduced cost. The efforts were made to find the liquid phase that melts at reduced temperature. The liquid phase includes Al<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub> system [2,3], Al-B-C [4], and Al<sub>2</sub>O<sub>3</sub>-rare earth oxide system [5-7]. However, the sintering below 1800°C was hardly successful.

The distribution of liquid phase can also affect the sintering of SiC. As the wet boundary enhances the kinetics of material transport, the even distribution of liquid is critically required for the successful sintering. Introduction of the sufficient liquid may certify wetting of boundary, however the excessive liquid phase deteriorates the mechanical properties such as creep resistance at an elevated temperature. Minimum liquid to wet the whole boundary should be the criterion to determine the ideal amount of liquid to introduce. For the even wetting, study is required concerning the heating schedule as well as the composition of the liquid itself. However, few

reports are available concerning the development of heating profile for the promotion of the even wetting.

Sintering schedule is often composed of multiple steps and thus the peak temperature is not same with the dwell temperature. The sintering is generally termed as two-step sintering [8]. The two step sintering can be applied to achieve dense structure with fine grains [9] or to reduce the sintering temperature [10]. In this work, two-step sintering route was tested to promote the even wetting and densification in SiC for the pressureless sintering at reduced temperature. The density and grain size of sintered SiC were compared with the conventionally sintered specimens. The results were discussed in terms of the behavior of liquid phase during the two-step sintering schedule.

## 2. Experimental

As a liquid former, 5.3 wt% of Al<sub>2</sub>O<sub>3</sub> (Sumitomo, Japan) and Y<sub>2</sub>O<sub>3</sub> (H. C. Starck, Germany) were mixed with SiC (crystal phase  $\alpha$ , Showa Denko, Japan). Al<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> were supposed to react with SiO<sub>2</sub> on the surface of SiC and to form 8 vol% of liquid phase. As a binder during forming, 3 wt% of polyethylene glycol were mixed with powder. The mixture was ball-milled for 48 hrs in ethyl alcohol. After milling, the mixture was dried at 85°C in a vacuum oven and passed through 125 mesh sieve. The obtained powder was uniaxially pressed and subsequently cold isostatically pressed at 150 MPa. The green body was sintered in 1 atm of flowing Ar gas.

The sintering was carried out either in conventional or two-step sintering route. The dwell temperature in conven-

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tional sintering (CS) was from 1700 to 2000°C. Temperature increased to 400°C at 3°C/min and kept for 1 h to remove binder. Subsequently, the specimens were heated at 10°C/min to the final sintering temperatures and kept for 1 h. In case of the two-step sintering (TSS), the heating schedule was same with the conventional sintering until 1000°C. Then the specimen was rapidly heated at 20°C/min to 2000°C. Upon reaching 2000°C, the specimen was quenched to the dwell step at 1700 or 1750°C and kept for 1 h. The specimen was named after its sintering route and dwell temperature. For instance, TSS-1750 represented a specimen held at 1750°C by two step sintering.

Densities of the sintered specimens were measured using Archimedes immersion technique. The mass of the specimen was measured before and after sintering to estimate the loss of weight.

The sintered specimens were then fractured for the microstructural analysis. Scanning electron microscopy (JSM-6300, JEOL, Japan) was used at 20 kV for the microstructural observation on fractured surface. The sintered surface was ground about 0.5 mm and sequentially polished with diamond pastes (9, 3, and 1 μm). Hardness and fracture toughness were determined using Vicker's indenter (AVK-C100, Akashi, Japan) by applying 5 kgf for 15 seconds on the polished surface. By measuring the crack lengths, the fracture toughness was calculated based on the report [11].

### 3. Results and discussion

The densities of sintered SiC specimens are shown in Fig. 1. In the CS series, the increase in density is evident with the sintering temperature, particularly between 1700 and 1800°C. Slight decrease in density was observed with the increase in temperature above 1850°C. The densities obtained by TSS were same with the best density from CS series. As the densities of TSS-1700 and TSS-1750 are superior to that of TSS-0 (no dwell step), the increase in density was considerable during the dwell step in the TSS.

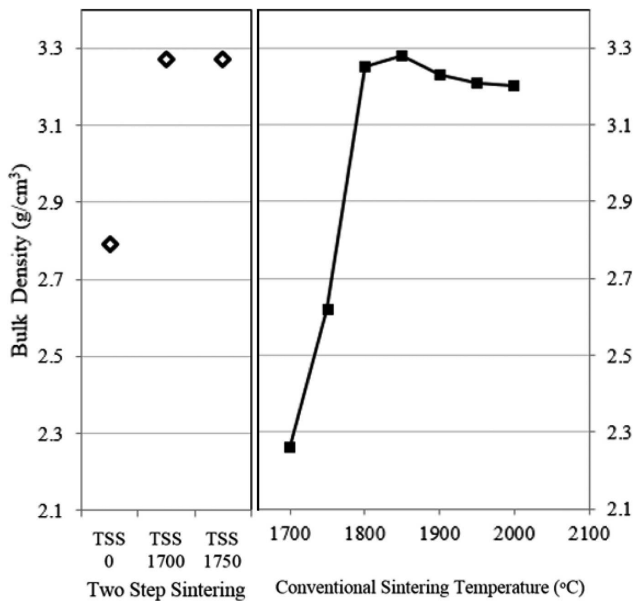


Fig. 1. Densities of sintered SiC with sintering route and dwelling temperatures

The weight losses with sintering conditions are shown in Fig. 2. The loss of mass was 5% in the CS at 1700°C. With the increase in sintering temperature, the loss of mass increased up to 20% at 2000°C in the CS series. On the contrary, the losses of mass were ranged at 6~7% in the TSS series, in spite of the peak temperature at 2000°C.

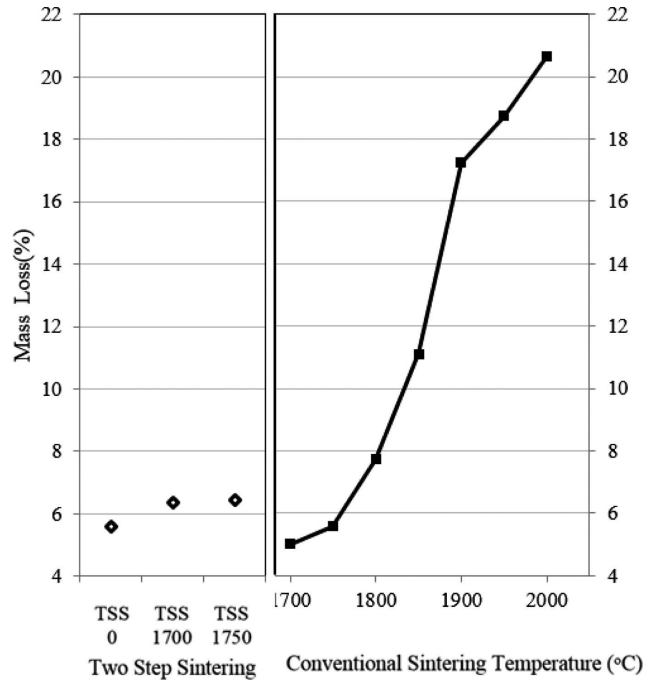


Fig. 2. Loss of mass in sintered SiC with sintering route and dwelling temperatures

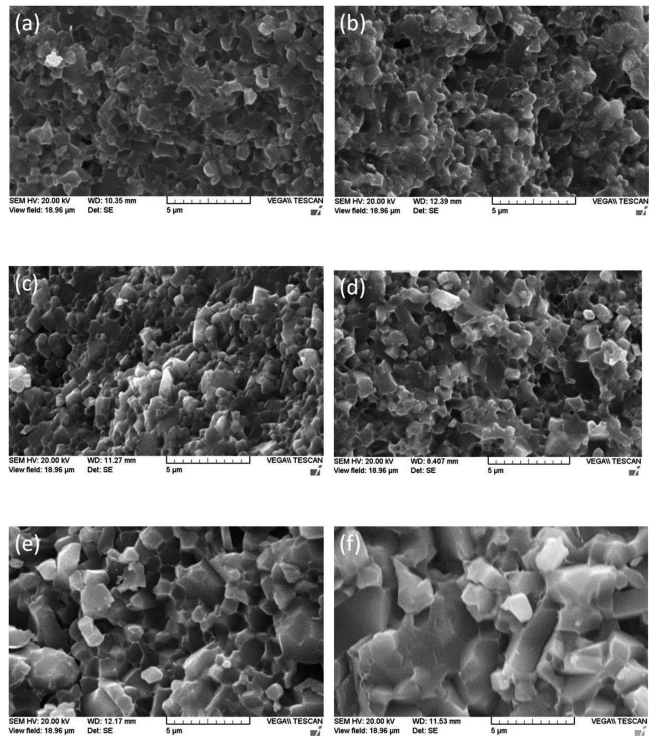


Fig. 3. Microstructures of sintered SiC with sintering route and dwelling temperature (a) TSS-1700, (b) TSS-1750, (c) CS-1800, (d) CS-1850, (e) CS-1950, (f) CS-2000

Fig. 3 shows the microstructures of SiC with the sintering conditions. TSS-1700 (Fig. 3a) and TSS-1750 (Fig. 3b) have the grains less than  $1\ \mu\text{m}$ . The existence of the liquid phase can be also observed. In the CS series (Fig.3c~f), the grain size increased with the sintering temperature, some of sintered specimens have angular grains greater than  $3\ \mu\text{m}$  depending on the sintering temperatures (c:1850°C, d:1900°C, e:1950°C, and f:2000°C). Fig. 1 and Fig. 3 show that the TSS could provide a dense specimen with fine grains.

Hardness of SiC specimens are drawn in Fig. 4 with sintering conditions. The TSS-1700 exhibited superior hardness ( $2321\pm 20\ \text{kgf/mm}^2$ ) compared with the rest. With the increase in sintering temperature, the hardness generally decreased. The CS-2000 exhibited hardness less than  $1900\ \text{kgf/mm}^2$ . The fracture toughness of SiC specimens are shown in Fig. 5. The best toughness was observed at CS-1950 ( $4.53\pm 0.07\ \text{MPa m}^{1/2}$ ). The toughness of TSS-1700 and TSS-1750 were smaller as  $3.54\pm 0.08$  and  $3.36\pm 0.04\ \text{MPa m}^{1/2}$ , respectively.

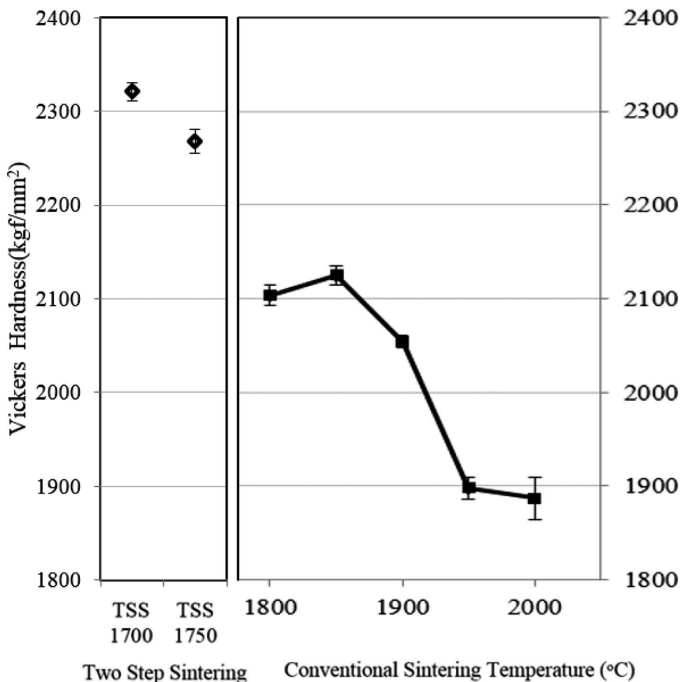


Fig. 4. Hardness of sintered SiC with sintering route and dwelling temperatures

According to the results in Fig. 1~5, the application of the TSS with dwelling at 1700°C could produce a dense specimen with fine grains and suppressed loss of mass. The specimen exhibited superior hardness than any other specimen in this work. The benefit of the TSS was sought in terms of the role of the liquid phase. The liquid phase facilitates the rapid transport of material via solution and precipitation route. The diffusion through the liquid phase is known to be much faster than that through the grain boundary [12]. As a result of the material transport via liquid phase, the grain can experience both change of shape and coarsening. The change of shape can result in increase in density by the elimination of pores among the grains. On the contrary, the coarsening merely wastes the driving for the densification. For the effective accommodation of shape, the liquid phase needs to evenly cover the surface of particles. Plus, the liquid phase needs to be conserved for a sufficient time to provide a channel for material transport.

Comparing the density of TSS-0 and TSS-1700 at Fig. 1, the sustained liquid is found to play a significant role in the densification.

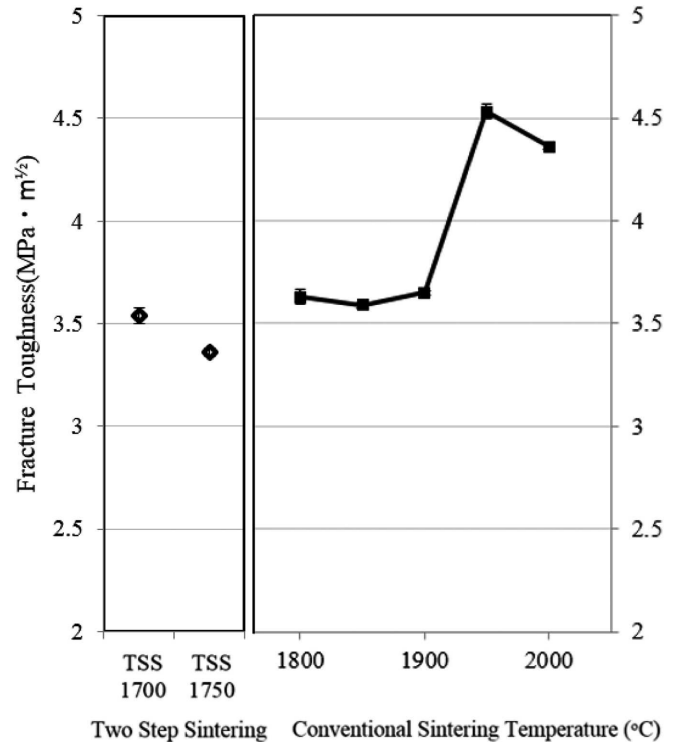


Fig. 5. Fracture toughness of sintered SiC with sintering route and dwelling temperatures

In this work, the specimens were rapidly heated to the peak temperature of 2000°C and immediately cooled to 1700~1750°C for dwelling. The even cover by liquid can be promoted by high capillary driving force and low viscosity, which is enhanced at elevated temperature. Thus rapid heating to 2000°C was applied at the first step of sintering. However, at this elevated temperature, the evaporative loss of liquid phase cannot be avoided. As Fig. 2 indeed shows, the loss of mass increased with temperature.

The quenching from 2000°C to 1700°C or 1750°C in the TSS thus reduces the evaporative loss of liquid and preserves the channel for rapid mass transport. Consequently, as Fig. 2 and 3 shows, application of the TSS could effectively suppress the evaporative loss and coarsening, while achieving the densification. In this study, the heat treatment schedule was designed for both even wetting of grain boundary and reduction of evaporative loss. The application of the TSS showed fine and dense microstructure exhibiting good hardness.

#### 4. Conclusions

The TSS route was designed and applied to obtain SiC with fine grains by promoting the role of liquid phase, which consists of 8 vol% of  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ . The SiC green bodies were rapidly heated to the peak temperature of 2000°C for even cover by the liquid. To suppress the evaporative loss of liquid, the specimens were immediately quenched from 2000°C to 1700 or 1750°C and kept for 1 h. The application of the TSS effectively suppressed loss of mass and coarsening.

The resultant SiC specimen was thus dense and composed of fine grains exhibiting good hardness.

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#### REFERENCES

- [1] S.J. Dapkunas, Am. Ceram. Soc. Bull. **67**, 388 (1988).  
 [2] D. Sciti, A. Bellosi, J. Mater. Sci. **35**, 3849 (2000).  
 [3] C.Y. Liu, W.H. Tuan, S.C. Chen, Ceram. Int. **39**, 8253 (2013).  
 [4] Y. Zhou, H. Tanaka, S. Otani, Y. Bando, J. Am. Ceram. Soc. **82**, 1959 (1999).  
 [5] H. Liang, X. Yao, J. Zhang, X. Liu, Z. Huang, J. Euro. Ceram. Soc. **34**, 831 (2014).  
 [6] F. Rodriguez-Rojas, A.L. Ortiz, F. Guiberteau, M. Nygren, J. Euro. Ceram. Soc. **30**, 3209 (2010).  
 [7] E. Ciudad, O. Borrero-Lopez, F. Rodriguez-Rojas, A.L. Ortiz, F. Guiberteau, J. Euro. Ceram. Soc. **32**, 511 (2012).  
 [8] I. W. Chen, X.H. Wang, Nature(London), **404**, 168 (2000).  
 [9] Y.I. Lee, Y.W. Kim, M. Mitomo, D.Y. Kim, J. Am. Ceram. Soc. **86**, 1803 (2003).  
 [10] B. Hwang, Y.-K. Paek, S.-H. Yang, S. Lim, W.-S. Seo, K.-S. Oh, J. Alloys Compd. **509**, 7478 (2011).  
 [11] B.R. Lawn, D.B. Marshall, J. Am. Ceram. Soc. **62**, 347 (1979).  
 [12] R.M. German, Liquid phase sintering, Plenum Press, New York 1985.