Effect of Nano-Yb$_2$O$_3$ addition on crystallization and sintering properties of fused quartz ceramic materials

Jinglong BU,¹ Yinglei GU, Min CHEN,² Yuejun CHEN and Zhifa WANG

Hebei Provincial Key Laboratory of Inorganic Nonmetallic Materials, College of Materials Science and Engineering, Hebei United University, Tangshan 063009, China
²School of Materials and Metallurgy, Northeastern University, Shenyang 110819, China

The effect of nano-Yb$_2$O$_3$ additive on crystallization and sintering behavior as well as its properties were investigated using fused quartz powder as raw material and nano-Yb$_2$O$_3$ as additive with dosages of 1% to 3% respectively after sintering at 1300 to 1400°C for 1 h. The results showed that cristobalite as the main crystal phase deposited while the sintering temperature was above 1300°C, and with increasing of sintering temperature, the amount of deposited cristobalite increased. Keiβite (Yb$_5$Si$_3$O$_9$) formed by reaction of added nano-Yb$_2$O$_3$ with SiO$_2$ not only restrained the crystallization of cristobalite, but also promoted densification of the materials by inhibiting grain growth of cristobalite. In addition, the addition of nano-Yb$_2$O$_3$ effectively decreased the expansion ratio of fused quartz ceramic materials during temperature elevating process by inhibiting crystallization of cristobalite, and the cold bending strength was slightly decreased due to the destruction of silicon-oxygen tetrahedron texture by addition of nano-Yb$_2$O$_3$.

©2013 The Ceramic Society of Japan. All rights reserved.

Key-words: Fused quartz materials, Nano-Yb$_2$O$_3$ addition, Sintering, Thermal expansion ratio, Crystallization

1. Introduction

Fused quartz ceramic materials are commonly manufactured using high-purity silica via melt-quench methods. As an amorphous material, it has with high viscosity and high energy, excellent properties such as low thermal expansion ratio, excellent thermal stability, low heat conductivity and high thermal shock resistance and so on, and is widely used in nuclear industry, aerospace, military, metallurgy, refractory and other fields.¹ However, when the products service at high temperature for a long time, partial fused quartz in the materials will crystallize and transferred to cristobalite, and the thermal expansion ratio of the material will increases, resulting in some excellent properties disappearing. Therefore, Inhibiting crystallization of fused quartz is a technical problem urgently to be solved.

Some early researchers discussed the crystallization behavior and crystallization kinetics of the fused quartz,²⁻⁷ and found that introducing conventional oxides and non-oxides as additives could inhibit crystallization and facilitate sintering of the fused quartz at some level,²⁻⁵ but the effect is not obvious. However, in the former work of our laboratory, we had discovered that there are markedly difference between non-nano and nano additives, which have different effect on crystallization and facilitate sintering of the fused quartz.¹⁰⁻¹⁴ Moreover, the reports about research on nano-Yb$_2$O$_3$ used as additive for inhibiting crystallization and facilitating sintering of fused quartz have not been found until now. Therefore, nano-Yb$_2$O$_3$ may have the better effect on inhibiting crystallization behavior and improving sintering performance of the fused quartz ceramic materials.

2. Experimental procedures

Fused quartz powder (d$_{50}$ = 19 μm, purity >99%) was used as main raw material and nano-Yb$_2$O$_3$ (size ≤ 40 nm, purity >99.9%) was used as additive to inhibit crystallization and facilitate sintering of fused quartz. Fused quartz powder and additive were mixed by wet ball blending machine in ethanol with zirconia balls for 2 h. After dried at 60°C for 24 h, the mixtures were molded to specimens with size of 52 mm × 10 mm × 10 mm under pressure of 50 MPa by a hydraulic press (NYL-300 hydraulic press machine). Finally the specimens were sintered in electric resistance furnace covered with graphite powder at temperature of 1300, 1350 and 1400°C for 1 h respectively. The dosages of nano-Yb$_2$O$_3$ additive in the samples were 1, 2 and 3%, and the samples were labeled as Y-1, Y-2 and Y-3, respectively, while the blank sample was labeled as B-0.

The sintered samples were characterized by apparent porosity, phase compositions, microstructure analyses, cold bending strength and thermal expansion ratio calculated according to Eq. (1). The apparent porosity were measured by immersion method in water under vacuum using Archimedes’ principle and calculated according to Eq. (2):¹⁵

\[
\text{Thermal expansion ratio} = \frac{L_2 - L_1}{L_1} \times 100\% \quad (1)
\]

where $L_1$ is the length before the change of temperature and $L_2$ is the length after the change of temperature.

\[
\text{Apparent porosity} = \frac{m_1 - m_3}{m_3 - m_2} \times 100\% \quad (2)
\]

Where $m_1$ is the mass of a dried sample in air (g), $m_2$ is the mass of the sample in water (g), $m_3$ is the mass of the sample with free bubbles on the surface (g).

Phase compositions were analyzed by X-ray powder diffraction (XRD, Cu target, 30 kV and 30 mA). The microstructure was observed by scanning electron microscopy (SEM) equipped with energy dispersive X-ray analyzer (EDX) on the fractured surfaces. The thermal expansion ratio was measured by PCY-high temperature horizontal dilatometer (with heating rate 5°C/min
before 300°C and 10°C/min after 300°C). And the cold bending strength was measured according Electric bending tester (DKJ-5000).

3. Results and discussion

3.1 Phase composition and microstructure

Figure 1 shows the XRD patterns of samples sintered at various temperatures. For the sample without addition [Fig. 1(a)], the hump-shaped peaks are observed, indicating that crystallization of cristobalite did not obviously occur at this temperature. In addition, keivite(Yb₂Si₂O₇) can be identified in samples with nano-Yb₂O₃ addition, indicating that keivite (Yb₂Si₂O₇) was formed by the reaction of SiO₂ with nano-Yb₂O₃ at the sintering temperature below 1300°C.

From Fig. 1(b), it is observed that the hump-shaped peaks disappeared and sharp crystallized SiO₂ (cristobalite) peaks was detected, indicating that crystallization reaction occurs obviously from 1350°C in the fused quartz materials, and the amorphous quartz has transferred to alpha cristobalite, then alpha type to beta one during cooling process. In addition, it is also observed that the intensity of cristobalite sharply decreased by addition of nano-Yb₂O₃. From Fig. 1(c), for the samples without addition and with 1% nano-Yb₂O₃ addition sintered at 1400°C, the intensity of cristobalite diffraction peak a little stronger than samples with 2 and 3% nano-Yb₂O₃ addition. This result indicates that the addition of nano-Yb₂O₃ additive still has some effects on restraining the crystallization of cristobalite in quartz ceramics materials at high temperatures, and this effect was enhanced with increment of nano-Yb₂O₃ dosage.

Figure 2 shows the microstructure of the samples sintered at 1400°C with different amount of nano-Yb₂O₃ dosage. For the sample without addition, loose microstructure with coarse grains (size of 50 μm) is observed, as shown in Fig. 2(a). While 1% nano-Yb₂O₃ was added, compact microstructure was observed, with the grain size decreased to about 30 μm [Fig. 2(b)]. Further increasing dosage of nano-Yb₂O₃ resulted more compact microstructure and smaller grain size [Figs. 2(c) and 2(d)]. The result indicates that nano-Yb₂O₃ addition has excellent effect on promotion of densification of the fused quartz materials by restraining the grain growth of deposited crystalline cristobalite.

It is considered that the effect of nano-Yb₂O₃ addition on promotion of densification was due to the binding effect of keivite(Yb₂Si₂O₇) on restraining the movement of cristobalite grain boundary and contributing to discharging of pores in the materials during densification process.

Regarding the effect of nano-Yb₂O₃ addition on inhibition of grain growth, it is considered that each quartz particle was uniformly coated with nano-Yb₂O₃ powder, the raw material of fused quartz ceramic is quartz glass powder that the surface network encounter breakage by crush silica glass, so it has high surface energy, and nano-Yb₂O₃ powder has higher surface energy than Yb₂O₃ with conventional size, therefore quartz
particle and nano-Yb2O3 powder easily bond together, and the breakage surface network of quartz particle is repaired by Yb2Si2O7 formed at high temperature, nano-Yb2O3 powder has smaller size than conventional Yb2O3 so that it easily repair the breakage surface network of quartz particle, and that’s why nano-Yb2O3 has more obvious effect on inhibiting crystallization of cristobalite than conventional Yb2O3. There is Yb2Si2O7 between each quartz particle restraining the SiO2 mass migration or movement of grain boundary, and adjacent grains connected to each othe, thus restraining the grain growth and promoting densification of the materials.

3.2 Sintering behavior

Figure 3 shows the apparent porosity of samples with different amount of nano-Yb2O3 addition after sintering at various temperatures for 1 h. The apparent porosities of samples sintered at various temperatures showed decreasing tendency with increment of nano-Yb2O3 addition, and the small amount addition was more effective. For the sample sintered at 1300°C without addition, the porosity was 34.6%, and it was decreased to 31.1% by addition of 1% nano-Yb2O3. For the sample sintered at 1400°C with 3% nano-Yb2O3 added, the porosity decreased to 14.3%. This result also indicates that nano-Yb2O3 addition has excellent effect on promoting densification of the fused quartz materials. Considering the effect of nano-Yb2O3 addition on promoting densification, the proper dosage is considered around 3%.

Regarding the effect of nano-Yb2O3 addition on promoting densification of the fused quartz materials, besides the effect of formed keiviite (Yb2Si2O7) on restraining grain growth of deposited cristobalite, it is considered that the promotion of densification was also contributed to the volume effect while the low density phase (cristobalite, with theoretic density of 2.2 g/cm³) transferred to high density phase (keiviite, with theoretic density of 5.95 g/cm³) that had 11% volume shrinkage.

3.3 Performance

Figure 4 shows the thermal expansion ratios during temperature elevating process for the samples with different dosages of nano-Yb2O3 additive sintered at various temperatures. It is well known that fused silica transformed to alpha cristobalite during sintering process, then cristobalite turned from alpha type to beta one during cooling process. On the contrary, beta cristobalite in the sintered samples would transfer to alpha type at temperature range of 180 to 270°C during temperature elevating process, accompanying with 2.8% volumetric expansion. While elevating temperature to the range of 800 to 900°C, alpha quartz transferred to tridymite, accompanying with 12.7% volumetric expansion. As a result, for the sample sintered at 1300°C, two peaks are observed in every thermal expansion curves at the above temperature range, regardless of the sample with nano-Yb2O3 addition or not, as shown in Fig. 4(a). For there was little cristobalite deposited from the sample sintered at 1300°C, there is little difference in thermal expansion curves is observed in Fig. 4(a).

For the samples sintered at 1350°C without nano-Yb2O3 addition, since there was a large amount of beta cristobalite (as described in Fig. 1), a typical thermal expansion curve with sharp volume expansion ratio of 1.5% is observed at temperature range of 180 to 270°C due to the transition of beta cristobalite to alpha one, as shown in Fig. 4(b). And a slight linear volume expansion is observed during further temperature elevating process, without volume expansion peak formed at temperature range of 800 to 900°C, indicating that the transition of alpha quartz to tridymite did not occurred for the sample sintered at 1350°C.

Increasing of temperature accelerates crystallization of the fused quartz ceramic materials, nano-Yb2O3 has different effect on inhibiting crystallization behavior with varying sintering temperature, however, crystallization from fused quartz glass to
alpha cristobalite at high temperature results in change of thermal expansion rate of fused quartz ceramic. For the sample with addition of nano-Yb$_2$O$_3$, a small thermal expansion ratio less than 0.2% is observed, indicating the excellent effect of nano-Yb$_2$O$_3$ on inhibiting volume expansion of quartz ceramics materials. The decrease of thermal expansion ratio by addition of nano-Yb$_2$O$_3$ is considered due to the binding effect of formed keivite that effectively inhibited the transition of fused quartz to alpha cristobalite, also is to decrease the volume expansion ratio of beta cristobalite transfer to alpha type at temperature range of 180 to 270°C. Therefore, it is can be concluded that the addition of nano-Yb$_2$O$_3$ not only promoted densification of quartz ceramics materials, but also could inhibit fused quartz transferring to alpha cristobalite. It is also observed from Fig. 4(b) that thermal expansion ratios of sample Y-1, Y-2 and Y-3 are very close to each other, indicating that the dosage of 1% is proper for the sample sintered at 1350°C.

For the sample sintered at 1400°C without nano-Yb$_2$O$_3$ addition [Fig. 3(c)], the thermal expansion curve is very similar to that of the sample sintered at 1350°C. But for sample with addition, due to the larger tendency of beta cristobalite transferring to alpha one, a volume expansion ratio of 1.1% is observed for the sample with 1% nano-Yb$_2$O$_3$ added. While 2% increasing nano-Yb$_2$O$_3$ was added, the volume expansion ratio was decreased to 0.6% before the curve turns to flat, and further increasing addition to 3% shows little more effect on decreasing of expansion ratio. Therefore, it is can be concluded that more dosage of nano-Yb$_2$O$_3$ addition is necessary with increment of sintering temperature to inhibiting this phase transition, and 3% of nano-Yb$_2$O$_3$ addition is considered proper for the sample sintered at 1400°C.

Figure 5 shows the cold bending strength of the samples sintered at various temperatures. It is well known that the bending strength of materials is dependent to the integrity of structure, phase composition and compactness. While the fused quartz ceramics material in present work was sintered at high temperature, the crystallized cristobalite fractured the integrity of the silicon-oxygen tetrahedron texture in amorphous quartz ceramics materials. In addition, the plastic deformation formed in the crystallized cristobalite under load further weakened the bonding of crystalline cristobalite. As a result, the cold bending strength was decreased with increment of sintered temperature, and it decreased from 16.5 to 9.6 MPa for the sample without nano-Yb$_2$O$_3$ addition while the sintered temperature increased from 1300 to 1400°C. And while nano-Yb$_2$O$_3$ was added, the formed fine dispersed keivite particles further destructed the integrity of the silicon-oxygen tetrahedron texture, with cold bending strength decreased. Therefore, it is considered that the cold bending strength of the fused quartz ceramics materials was mainly dependent to the integrity of the silicon-oxygen tetrahedron texture, and it would be decreased by addition of nano-Yb$_2$O$_3$ though the densification would be promoted.

4. Conclusions

The present work investigated the effect of nano-Yb$_2$O$_3$ addition on sintering behavior and properties of fused quartz ceramic materials. Based on the above results, the following conclusions could be drawn.

(1) Cristobalite as the main crystal phase would crystallized in the fused quartz glass materials while the sintering temperature was above 1300°C, and with increasing of sintering temperature, the amount of cristobalite was increased.

(2) The added nano-Yb$_2$O$_3$ reacted with SiO$_2$ and keivite (Yb$_2$Si$_2$O$_7$) formed, which not only restrained the deposit of cristobalite, but also effectively promoted densification of the materials by inhibiting grain growth of cristobalite. And with increasing dosage of nano-Yb$_2$O$_3$, its effect was enhanced.

(3) The addition of nano-Yb$_2$O$_3$ effectively decreased the expansion ratio of the fused quartz ceramic materials during temperature elevating process by inhibiting crystallization of cristobalite, and with increment of sintering temperature, the dosage of nano-Yb$_2$O$_3$ necessary to keep the fused quartz ceramic materials with a low expansion ratio was increased.

(4) Cold bending strength of the fused quartz ceramic materials was mainly dependent to the integrity of the silicon-oxygen tetrahedron texture in the microstructure. It was decreased with increasing of sintering temperature due to the crystallization of cristobalite, and was further decreased by the addition of nano-Yb$_2$O$_3$ though the compactness was slightly increased.

Acknowledgment The authors acknowledge the financial support from the National Natural Science Foundation of China (51072046, 51174049).

References
1) X. D. Yuan, W. L. Cui and W. H. Liu, Glass (China), 26, 44–46 (1999).
2) N. V. Garibina, V. K. Pavlovskii and A. D. Semenov, Glass Ceram., 55, 319–325 (1998).
3) Y. W. Ling and H. H. Min, Ceram. Int., 21, 187–193 (1995).
4) Z. Zhang, Aerosp. Mater. Technol. (China), 20, 54–59 (1990).
5) F. E. Wagstaff, J. Am. Ceram. Soc., 52, 640–656 (1969).
6) V. K. Leko and L. A. Komarova, Inorg. Mater., 11, 1743–1766 (1975).
7) G. W. Wen, T. Q. Lei and Y. Zhou, Mater. Sci. Technol. (China), 9, 1–5 (2001).
8) S. Y. Nan, J. L. Bu, Z. F. Wang, Z. X. Zhao, Y. L. Gu and H. F. Ma, J. Hebei Polytech. Univ. (Natural Science), 31, 95–98 (2009).
9) Z. B. Zhao, F. T. Liu, C. Z. Wu, F. Sun and X. D. Yuan, Bull. Chin. Ceram. Soc., 29, 1145–1148 (2010).
10) F. Ma, Z. F. Wang, J. L. Bu, R. L. Wang and S. S. Chen, Adv. Mater. Res., 97–101, 880–883 (2010).
11) Y. W. He, Z. F. Wang, F. Ma, J. L. Bu, H. Y. Zhao and R. L. Wang, Adv. Mater. Res., 150–151, 1786–1789 (2011).
12) J. L. Bu, F. Ma, Y. H. Zhang, H. Y. Zhao, R. L. Wang and Z. F. Wang, Adv. Mater. Res., 150–151, 1782–1785 (2011).
13) Y. J. Chen, Z. F. Wang, J. L. Bu, L. X. Yu, R. L. Wang and R. S. Wang, Adv. Mater. Res., 295–297, 1418–1421 (2011).
14) Y. J. Chen, Z. F. Wang, L. X. Yu, J. L. Bu, R. L. Wang and R. S. Wang, Adv. Mater. Res., 335–336, 695–698 (2011).
15) M. Chen, C. Y. Lu and J. K. Yu, J. Eur. Ceram. Soc., 27, 4633–4638 (2007).