Experimental Design Applied to Silicon Carbide Sintering

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Silicon carbide is a promising structural ceramic used as abrasives and applied in metallurgical components, due to its low density, high hardness, and excellent mechanical properties. The composition and content of the additive can control liquid-phase sintering of SiC. Compositions based on the SiO$_2$-Al$_2$O$_3$-RE$_2$O$_3$ system (RE = rare earth) have been largely used to promote silicon carbide densification, but most studies are not systematically presented. The aim of this work is to study the effect of several oxide additives in the SiO$_2$-Al$_2$O$_3$-Y$_2$O$_3$ system on the densification of silicon carbide using experimental design. This technique seems to be effective in optimizing the values of maximum density with minimum weight loss.

I. Introduction

Silicon carbide is considered an important structural ceramic due to its unique properties, such as low density, high hardness, and high mechanical and wear resistance. This material can be used in several applications, such as abrasives, refractories, electrical/electronic components, and metallurgical applications.

Sintering of silicon carbide can occur by different processes: in the solid state, with boron or carbon addition or in the presence of a liquid phase with metallic oxide addition. The liquid phase should have suitable characteristics for promoting densification. The specific surface area of silicon carbide raw material, the sintering atmosphere, time and temperature, and, particularly, the additive composition are important variables that can control the liquid-phase sintering.

The choice of additive composition is usually made empirically, on the basis of phase diagram considerations. However, this approach has not shown direct correlation to densification data. Due to this, an attempt to systematically evaluate the composition can be made through statistical planning of experiments, i.e., experimental design.

Experimental design is a statistical method used to determine the relations between the response and the set of experimental variables that possibly have an influence on this response. Through this method, it is possible to establish a set of experimental variables that produce the best response values. The mixture design is usually represented as a surface diagram, from which the influence of the composition can be estimated.

After choosing the set of experiments that allows suitable and reliable measurements of the variable, fitting of the collected data on the basis of mathematics models should be done with the help of hypothesis tests. These models can be linear, quadratic, cubic, or special cubic, and they describe the behavior of the studied process, within the chosen experimental region.

In general, more than one additive is used in silicon carbide sintering using liquid phases. In these cases, the corners of the experimental region do not correspond to the pure components. Therefore, pseudocomponents should be used.

Compositions based on the SiO$_2$-Al$_2$O$_3$-Y$_2$O$_3$ system have been largely used to densify silicon carbide ceramics, although most studies are not presented in a systematic form. The objective of this work is to use techniques of experimental design to study the effect of the initial composition on the densification of silicon carbide ceramics, using SiO$_2$-Al$_2$O$_3$-Y$_2$O$_3$ as the additive system. The results were evaluated through measurements of densities and temperatures of maximum shrinkage.

II. Experimental Procedure

To study the sintering behavior of silicon carbide based ceramics, alumina (Al$_2$O$_3$, Alcoa, A-16 SG, 99.9%), silica (SiO$_2$, Fluka), and yttria (H. C. Starck, grade C, 99.99%) were selected as sintering additives. The (3,2) centroid design was applied, considering pseudocomponents $X_1 = $ SiO$_2$, $X_2 = $ Y$_2$O$_3$, and $X_3 = $ Al$_2$O$_3$ and using 20–60 mol% of each pseudocomponent. The compositions used are presented in Fig. 1(a). Compositions 2 and 4 were done to verify the validity of the mathematical model. The experimental region studied in this work, based on the SiO$_2$-Al$_2$O$_3$-Y$_2$O$_3$ system, is indicated in Fig. 1(b).

The additives were mechanically homogenized for 4 h. A 10 mol% amount of the additives was added to silicon carbide (SiC, H. C. Starck, BF-17, 91.9% B), which was then mixed in an attritor for 4 h. The mixtures were dried in a rotoevaporator and uniaxially pressed at 20 MPa. These specimens were then cold isostatically pressed at 200 MPa.

Sintering experiments were done in a dilatometer (Netzsch, DIL, 402) to evaluate the maximum shrinkage temperatures and the kinetic behavior of silicon carbide sintered with oxide additives. Sintering was conducted with argon flow, and a heating rate of 15°C/min was applied up to 1950°C, keeping this dwell temperature for 1 h.

The same sintering cycle was selected to sinter samples in a graphite resistance furnace (Astro), using a protective powder bed of 10 vol% 60SiO$_2$·20Y$_2$O$_3$·20Al$_2$O$_3$ composition and 90% SiC to cover the samples in a graphite crucible. The samples were characterized by density measurements using Archimedes method and by weight loss evaluation. The Design Expert software was used to obtain the surface response and level curves of studied variables. The special cubic model was applied.

III. Results and Discussion

To verify the reliability of the surface response methodology used in this work, the liquidus temperatures of all seven compositions (except 2 and 4) were estimated using the SiO$_2$-Al$_2$O$_3$-
Fig. 1. (a) Compositional diagram (mol%) showing the compositions used. (b) SiO$_2$-Al$_2$O$_3$-Y$_2$O$_3$ phase diagram (after Ref. 19), indicating the pseudocomponents region used in the mixture design.

Fig. 2. Response surface of the liquidus temperature obtained from the SiO$_2$-Al$_2$O$_3$-Y$_2$O$_3$ phase diagram.

Y$_2$O$_3$ phase diagram. The response surface of the liquidus temperature is shown in Fig. 2. Comparing Fig. 1(b) and Fig. 2, one can notice that this methodology produces level curves that are in good agreement with those predicted in the phase diagram, although it is not possible to estimate the eutectic temperature by mixture design.

Figure 3 shows typical behavior of dilatometric experiments. Three peaks of maximum shrinkage rates can be seen (Fig. 3(b)). The first peak occurs at $\sim$1300°C, the second at $\sim$1700°C, and the last one at $\sim$1800°C. Details of this behavior are reported elsewhere. The critical shrinkage peak occurs at $\sim$1800°C, hereafter labeled T1. Above this temperature, the shrinkage rate decreases, although microstructural changes are still taking place.

Figure 4 shows the response surface of the T1 temperature, considering a range from 20 to 60 mol% of each component (SiO$_2$, Y$_2$O$_3$, and Al$_2$O$_3$) in the mixture. This temperature indicates that the critical process occurs in the range of approximately 1700–1840°C, without correlating to the liquidus temperature. The temperature T1 should be minimized so that the process to obtain high-density ceramics becomes more efficient and economical.

Figure 5 shows the response surface of density values from silicon carbide sintered in a graphite resistance furnace at 1950°C/h. It can be seen that densities higher than 91% theoretical densities can be obtained for all of the compositional range determined in the mixture design. The highest density values are $\sim$96.7% theoretical densities. Figure 6 represents the response surface obtained from weight loss values of the same sintered sample. Weight loss of 4.5–8% can be obtained using a protective powder bed to cover the samples during sintering in a graphite resistance furnace. It is desirable that the samples have higher density with lower weight loss. From a comparison of the level curves of density and weight loss in Figs. 5 and 6, it can be seen that the best composition of additives points toward (0.1991, 0.3584, 0.4425), which corresponds to 26.5 mol% SiO$_2$, 35 mol% Y$_2$O$_3$, and 38.5 mol% Al$_2$O$_3$ in the SiO$_2$-Y$_2$O$_3$-Al$_2$O$_3$ phase diagram, with an estimated variation of $\sim$5%. This optimized composition is not near the eutectic composition, as would be expected from consideration of the literature.
The composition that has the higher density with the lowest weight loss has a Ti temperature higher than 1800°C. The densification process seems to be effective, even though it occurs at a relatively high temperature.

IV. Conclusions

Suitable additive compositions in the SiO$_2$-A1$_2$O$_3$-Y$_2$O$_3$ system (10 mol%) are used for sintering silicon carbide, reaching densities up to 95% theoretical density. The mixture design applied in this work can be successfully applied to estimate the trends and the best results of densities and weight loss of compositions on the basis of the SiO$_2$-Y$_2$O$_3$-A1$_2$O$_3$ phase diagram to obtain high-density silicon carbide ceramics.

References
