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INFLUENCE OF Si-POWDER CHARACTERISTICS ON THE PORE STRUCTURE OF Si-POWDER COMPACTS AND OF REACTION-BONDED Si₃N₄

H.-J. KLEEBE and G. ZIEGLER

Deutsche Forschungs- und Versuchsanstalt für Luft- und Raumfahrt, Institut für Werkstoff-Forschung, D-5000 Köln 90, F.R.G.

Abstract - In order to achieve a homogeneous starting material for the production of dense Si₃N₄ by post-sintering of RBSN, the morphological and chemical characteristics of the Si-starting powders as well as the pore structure of the Si-powder compacts have to be optimized. In this context, the influence of the grain size distribution on the micropore size distribution of the Si-powder compacts was determined through a systematic variation of the grain size distribution by dry and wet milling. The effect of micropore structure of the Si-powder compacts on the micropore size distribution of RBSN was analyzed.

I - INTRODUCTION

Post-sintering of reaction-bonded Si₃N₄ (RBSN) is a promising technique for producing dense Si₃N₄ materials and components /1-3/. Consequently, in this two-step-process the optimization of the starting RBSN with the addition of sintering additives is of interest. Results can be used to improve RBSN as engineering material for a wide variety of high-temperature structural applications, too /4/. For both routes the microstructure and the resulting mechanical properties are strongly influenced by the chemical and morphological characteristics of the Si-starting powders and the pore structure of the Si-powder compacts. Thus, it is important to know the influence of Si-powder characteristics and pore structure of Si-powder compacts on the microstructure and mechanical properties of RBSN /5-9/. In this paper, the first step, the influence of Si-powder characteristics on the micropore structure of Si-powder compacts and of RBSN, is discussed. In this context, the influence of the particle size distributions of one Si-starting powder (changed by dry and wet milling) as well as of different commercially available Si-powders (as received) on the green density and micropore size distribution of the Si-powder compacts was investigated. The resulting micropore structure of RBSN is correlated to the micropore size distribution of the Si-powder compacts.
II - EXPERIMENTAL PROCEDURE

The particle size distribution of a commercially available Si-powder (powder A in Table 1) was systematically changed by wet (in isopropanol) and dry milling in a planetary mill. The milling time was increased in steps of 5 and 10 hours up to 50 hours maximum. In order to avoid metallic contamination, the mill and the grinding balls used were made of Si₃N₄. The particle size distributions of the different Si-powders were determined by a sedigraph micromeritics 5000. The chemical characteristics of Si-powder A and other commercially available Si-powders investigated are given in Table 1. Figure 1 shows the particle size distributions of commercially available Si-starting powders (as received) investigated.

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<td>milling experiments</td>
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Table 1 - Chemical composition of various commercially available Si-starting powders.

Fig. 1 - Particle size distributions of various commercially available Si-starting powders (see also Table 1).

Si-powder compacts were prepared by uniaxial and cold isostatic pressing, applying pressures up to 2500 bars. Pore size distributions of the Si-powder compacts and the resulting RBSN-materials were determined by mercury pressure porosimetry. All specimens were nitrided under identical conditions (maximum temperature 1430 °C, atmosphere 90 vol.% N₂ and 10 vol.% H₂ at constant nitriding pressure of 950 mbar, nitriding time 120 hrs).
III - RESULTS

Influence of milling conditions on Si-powder characteristics

The particle size distributions resulting from wet and dry milling of the Si-powder A are given in Figure 2. Generally, the increase of grinding time leads to smaller particle diameters in both cases, but does not essentially change the characteristics of the particle size distributions neither by dry nor by wet milling. Wet milling produces a narrower particle size distribution compared with dry milling.

![Particle size distributions resulting from wet and dry milling of Si-powder A.](image)

Fig. 2 - Particle size distributions resulting from wet and dry milling of Si-powder A.

The decreasing particle size with increasing grinding time is indicated by changes of the specific surface area (Figure 3).

![Increase of specific surface area and oxygen content with increasing grinding time.](image)

Fig. 3 - Increase of specific surface area and oxygen content with increasing grinding time.

There are only minor differences in the specific surface area between dry and wet milling. In most cases, the specific surface area after wet milling is a little smaller than after dry milling. Wet milling has the effect that particularly the large particles are more reduced compared with dry milling (see upper part of Figure 2). Therefore, dry milling produces a broader particle size distribution and due to the increase of fine particles a slightly larger specific surface area.

During milling the oxygen content increases simultaneously with the specific surface area of the Si-starting powder for both types of milling. However, the oxygen content of the dry milled Si-powder is about twice as high as of the wet milled powder (Figure 3).
Influence of Si-powder characteristics on density and micropore structure of the Si-powder compact

With increasing specific surface area (grinding time) the green density of compacts made of wet and dry milled powders increases, runs through a maximum and decreases to lower values. Si-powder compacts prepared with dry milled powders show a higher green density compared with wet milled powders. Under the compaction conditions used, green densities of wet milled powders vary between 1.43 and 1.56 g/cm³, of dry milled powders between 1.56 and 1.70 g/cm³. The compactibility of Si-powders is strongly influenced by the particle size distribution of the Si-powders. Here, the broader distribution of dry milled powders gives better results. Very fine powders are more difficult to compact and lead to rather low green densities.

Pore size distributions of various Si-powder compacts prepared with dry and wet milled Si-powders are shown in Figure 4. With decreasing particle size, respectively increasing specific surface area of the Si-powders the pore size distributions are shifted to smaller pore diameters, but the curve characteristics do not change essentially. The Si-powder compacts of wet milled Si-powders (narrow particle size distribution) show a broader pore size distribution. On the other side, however, a narrow pore size distribution can be achieved by compacting Si-powders with a broad particle size distribution, e.g. dry milled powders, as they lead to a better space filling and thus to a higher green density of the Si-powder compacts.

![Graph showing pore size distributions of Si-powder compacts](image)

Fig. 4 - Pore size distributions of Si-powder compacts and resulting RBSN-grades prepared with wet and dry milled Si-powders.

Influence of micropore structure of the Si-powder compacts on the micropore structure of RBSN

The density of RBSN directly depends on the green density of the Si-powder compacts. Therefore, the higher green density of the dry milled powders results in a higher density of the RBSN-grades. When comparing the pore size distribution of the Si-powder compacts with those of the nitried samples two aspects are to be considered. First, looking at the Si-powder A, processed by different preparation methods (dry and wet milling), the characteristic pore size distribution and the sequence of the Si-powder compacts can be found again in the RBSN-grades, only shifted to smaller pore sizes (Figure 4). In this case, the micropore size distribution of the nitried sample reflects the micropore structure of the Si-powder compact. Therefore, the powder characteristics, especially the particle size distribution, has a strong influence on the micropore size distribution of RBSN. Second, comparing the pore size distributions in Si-powder compacts made from different commercially available Si-powders with the pore structure in these specimens after nitridation, it may be concluded that not only the particle size distribution and the fineness of the starting powder are of importance, but that also the chemical characteristics of the Si-
powders have a strong influence on the micropore size distribution of the RBSN grades (Figure 5). It is obvious that in this case the micropore structure of the Si-powder compacts does not only reflect the micropore structure of the RBSN-materials. In particular, the Si-starting powder D with a broad particle size distribution (see Figure 1), a high green density and a narrow micropore size distribution of the powder compact, but a rather high metallic element concentration (see Table 1), shows after nitridation large micropores compared to powders A and B. Therefore, when evaluating different Si-starting powders it is important to have a close look at the chemistry of the Si-powder, because a higher amount of metallic impurities obviously creates an unfavourable micropore structure (and macropores) in the RBSN-grades.

Fig. 5 - Pore size distributions of Si-powder compacts and resulting RBSN-grades prepared with commercially available Si-powders.

IV - SUMMARY

Processing of Si-starting powders by milling leads to an essential reduction of the particle size, consequently to an increase in the specific surface area, but also to rising oxygen contents. Dry and wet milling produces different particle size distributions. The pore structure of the Si-powder compact is controlled by the particle size distribution of the Si-starting powder. A broad particle size distribution produced by dry milling results in a better compaction behaviour of the Si-powder and smaller micropores in the Si-powder compacts. After nitridation, the micropore size distribution of the RBSN-samples reflects the micropore structure of the green Si-compacts prepared from the same Si-powder after different processing steps. However, using various commercially available Si-starting powders, it is not only the particle size distribution and the fineness, but also the chemical characteristics of the Si-powders that have a strong influence on the resulting micropore structure of RBSN.

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