SINTERING OF SILICON NITRIDE AT ATMOSPHERIC PRESSURE

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ABSTRACT

It is well known that highly covalent materials like silicon nitride are difficult to densify by sintering. Even if considerable pressure is applied, as in hot-pressing, sintering aids, e.g., MgO, Y₂O₃, have to be employed.

Pressureless sintering generally requires a higher temperature than hot-pressing. However, during sintering at such high temperatures a weight loss occurs. This is due to dissociation of the silicon nitride and - what appears so far not to have been fully appreciated - loss of the volatile sintering aid, e.g. MgO. By suitable choice of a powder bed into which the samples are placed, dissociation and volatilization can be suppressed at atmospheric pressure of nitrogen, and high sintered densities can be obtained.

Because of the less drastic decay in strength at high temperatures of samples using Y₂O₃ rather than MgO as sintering aids, a composition 91% Si₃N₄ + 8% Y₂O₃ + 1% MgO has been chosen for the sintering study. High densities were achieved by sintering at 1800°C.

The same sintering aids can also be admixed to silicon before it is subjected to nitridation and final high temperature sintering at 1800°C. This process, which may also be described as "post-sintering of reaction sintered silicon nitride", has resulted in very high room-temperature (≈ 1000 MN/m²) with linear shrinkage of only about 6%.

It is also possible to carry out the post-sintering process on reaction-sintered silicon nitride to which no sintering aids have been added in powder form by transferring the sintering aid in the vapour form into the reaction sintered body. In this way
silicon nitride of density 3.05 Mg/m³ has been formed, which had a higher strength than the precursor reaction-sintered material between room temperature and 1400°C.

INTRODUCTION

Two types of silicon nitride are today commercially available i.e. reaction sintered (RSSN) and hot-pressed silicon nitride (HPSN). Their particularly advantages and disadvantages are well known. In the case of the rotor of a gas turbine both high strength and fabricability of complex shapes are required. This has led to the concept of the "duo-density" rotor which is made up of an injection-moulded RSSN blade ring and a HPSN central disc. The desirability of processing this component in one piece has directed present research effort towards sintering of silicon nitride (SSN). The problems of sintering silicon nitride have been discussed recently; they are i) low green density of highly sinterable silicon nitride powder resulting in high shrinkage, ii) dissociation of silicon nitride at sintering temperature, iii) volatilization of sintering aid. This paper shows how an appreciation of all the problems leads to a pressureless sintered silicon nitride of exceptional high strength at room temperature which has undergone only 6-7% linear shrinkage.

THE DISSOCIATION OF Si₃N₄ AND THE VOLATILIZATION OF MgO

The weight losses occurring during sintering of Si₃N₄ powder to which 5% MgO has been added and the corresponding sintered densities are shown in Figs. 1 and 2 for different sintering temperatures. Curves "a" which are due to Terwilliger and Lange who first reported the result of open sintering in nitrogen at atmospheric pressure. The high weight loss and the low density (< 80% theoretical) were ascribed entirely to the dissociation of Si₃N₄. Mitomo was able to obtain higher densities by suppressing the dissociation through sintering at a nitrogen pressure of 10 atm. Similar though slightly lower densities were obtained by sintering in a powder bed consisting of Si₃N₄ and BN (curves "c"). However, such samples were inhomogeneous and exhibited, on sectioning a 1.5 mm thick skin of lower density which by Laser Microspectral Analysis was shown to have a lower Mg content than the bulk of the sample (Fig. 3). This was evidence for loss of MgO from the surface and, in order to decrease it, MgO was incorporated in the powder bed which resulted in homogeneity and further improvement in the densification. The optimum sintering conditions and properties are given in Table 1. The additive Fe was the residue from milling in a steel mill. It is interesting that the iron is contained as an impurity phase which is a solid solution of fayalite and forsterite.