SYNTHESIS OF SILICON NITRIDE WHISKERS BY MICROWAVE HEATING

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ABSTRACT

Whiskers of silicon nitride were synthesized by heating silicon powder compacts, silicon single crystal and polycrystalline silicon in microwave in the presence of flowing forming gas or nitrogen. Various gas compositions and form of silicon used resulted in different whisker morphologies. Silicon powder as starting material leads to the formation of needle-like whiskers while silicon single crystal and polycrystalline silicon led to the formation of wool-like and web-like structures respectively. Length of the whiskers apparently depends on the holding time at the optimum temperature ~1350°C; whiskers up to 250 micrometers in length may be grown in 30 minutes. Microstructural data suggest that the silicon nitride whiskers form through gas-solid reaction and vapor-solid mechanism.

INTRODUCTION

Ceramic whiskers exhibit several useful properties such as high melting points, low densities and high moduli [1]; these make them useful as reinforcing components in composites, for increased fracture toughness [2]. The advantages of using ceramic whiskers in ceramic-matrix composites (CMC) and metal-matrix composites (MMC) have been reported [3-6]. Different reinforcing materials in different matrices is expected to provide specific advantages. The synthesis and use of various ceramic whiskers, such as Sic, TiC, Si3N4 and TiN, have therefore been investigated.

Routes to Si3N4 Whiskers

Several routes have been investigated for the synthesis of ceramic whiskers. In the case of Si3N4, Grilkov et al. have reported formation of Si3N4 whiskers from (SiO₂+Si) mixture in (N₂+H₂) atmosphere via the VLS mechanism involving Al-Si or Fe-Si alloy [7]. Hayashi et al. have reported growth of Si3N4 whiskers by nitridation of the SiO₂-C-NaAlF₄ system [8]. The yield composition was β-sialon (85%) + α-Si3N4 (15%), and there were indications of the VLS mechanism operating in this case too. A key factor for commercialization is cost effective process of synthesis, and this paper deals with a new and simpler route to Si3N4 synthesis.

EXPERIMENT

Silicon in powder and lump form was obtained from Alfa Chemicals Co. with respective purities of 99.5% and 99.9995%. Powder had a sieve classification of -325 mesh. Lump silicon was further polished with SiC paper to obtain flat smooth surfaces. Silicon single crystal (wafer) was 0.5mm thick. Silicon, in powder, monocrystalline and polycrystalline forms, were subjected to microwave heating for various periods and temperatures in a mixture of N₂ (95%) and H₂ (5%). The Si specimens were then examined in detail to study the effect of the microwave processing. Formation of whiskers was found to occur by this process,
optimum time, temperature and gas flow parameters, 30 min at 1350°C with 100sccm gas flow, were selected for comparative study of the effect of the different Si forms.

RESULTS

With Si Powder

Whiskers formed with Si powder were examined by SEM. Fig. 1a shows the general appearance of the specimens while Fig. 2a provides a better view of the individual whisker grown on silicon particle.

The whiskers are found to be straight, needle-like with sharp tips. No evidence for any metallic cap suggestive of the VLS mechanism operating was found. XRD analysis confirmed the presence of α-Si₃N₄.

With Monocristalline Si Wafer

Whiskers formed with Si monocristalline wafer are shown in Fig. 2a. The general appearance may be termed wool-like, with the individual characteristics showing longer and curved whisker formation (Fig. 2b).

Figure 1a,b. SEM images of powdered Si sample after heating in microwave for 30 minutes at 1350°C (N₂/H₂ gas).

Figure 2a,b. SEM images of single crystal Si sample after heating in microwave for 30 minutes at 1350°C (N₂/H₂ gas).
XRD analysis again confirms the presence of $\alpha$-Si$_3$N$_4$ (Fig. 3).

![X-ray diffractogram of Si single crystal after microwave heating](image)

Figure 3. X-ray diffractogram of the Si single crystal after microwave heating.

EDAX and TEM (SAEDP) analysis of several whiskers were also carried out. EDAX showed the whiskers to be generally Si rich. SAEDP analysis showed some of them to be amorphous, and others crystalline. The latter showed diffraction patterns in agreement with the XRD analysis.

**With Polycrystalline Si Block**

With polycrystalline Si, in addition to long and curly whiskers, web-like structures were found, as shown in Fig 4.

**CONCLUSIONS**

A simpler and effective process for synthesis of Si$_3$N$_4$ in whisker form has been successfully demonstrated. Silicon, in powder, monocristalline or polycristalline form, when subjected to microwave processing at 1350°C for 30 minutes in N$_2$ (95%) + H$_2$ (5%) gas mixture flowing at 100 sccm, can yield $\alpha$-Si$_3$N$_4$ whiskers. Upgrading this process could yield a more cost-effective route to $\alpha$-Si$_3$N$_4$ whisker synthesis and growth for practical applications.

![SEM image of the polycrystalline Si sample after heating in microwave for 30 minutes at 1350°C (N$_2$/H$_2$ gas)](image)

Figure 4. SEM image of the polycrystalline Si sample after heating in microwave for 30 minutes at 1350°C (N$_2$/H$_2$ gas).

**REFERENCES**