# CRITICAL FLAW SIZE REDUCTION IN COMMERCIAL $Si_3N_4$-TiN COMPOSITES FOR WEAR APPLICATIONS

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## ABSTRACT

Silicon nitride ($Si_3N_4$) based materials are used for engineering applications wear high performance in demanding environments is required. These applications included cutting tools and roller bearings. The addition of titanium nitride (TiN) particles into a $Si_3N_4$ matrix can lead to particle reinforcement behaviour resulting in improved mechanical properties including fracture toughness ($K_{Ic}$) and strength. Although the addition of TiN particles into the $Si_3N_4$ is relatively simple and can be performed without additional processing equipment, many potential problems can arise.

In the current work fine TiN particles were added to a $Si_3N_4$ matrix in 0, 10, 20 and 30 wt.% content. All materials were manufactured commercially. The $K_{Ic}$, Young's modulus and coefficient of thermal expansion (CTE) all showed a linear increase with TiN addition. However a similar trend as not observed in the average flexural strength as would be expected from the $K_{Ic}$ behaviour. Hence a detailed fractographical study was performed to determine the causes of failure. Fractography was performed as recommended in the European and American standards and combined with fracture mechanics to identify correctly the different types of fracture origins observed. In composites with low flexural strength, the fracture was attributed to TiN based clusters and agglomerates. In higher strength materials failure was due to traditional processing defects including porosity and machining marks. In conjunction with the manufacturer the size of the TiN related defects was reduced. It was possible to produce composites with increased strength but also with low strength deviation and a high Weibull modulus.

## 1 INTRODUCTION

The introduction of particles into a $Si_3N_4$ matrix is a cost effective method of increasing the $K_{Ic}$ performance of these brittle ceramics. No additional processing equipment is required and the powder does not have the associated health risks of fibres. The use of TiN particles has been shown to lead to improvements in $K_{Ic}$ and strength [1]. In addition TiN is also believed to alter the wear characteristics, and TiN coatings are often used on hard steel tooling. The mechanisms by which TiN increase the $K_{Ic}$ is thought to include microcracking, crack bowing, crack deflection and residual stresses [2]. In the current work mechanical properties of $Si_3N_4$-TiN based composites developed commercially are characterised. Fractography was used to identify the different types of fracture origins and to improve the processing of the composites. The aim was to reduce the critical size of the fracture defects and improve flexural strength without increasing the processing costs.

## 2 EXPERIMENTAL

$Si_3N_4$ and $Si_3N_4$-TiN composites produced with 10, 20, and 30 wt.% TiN content were purchased from FCT Technologie GmbH, Germany. Alumina and yttria were used sintering additives to hot-press discs of 220 mm diameter x 6 mm thickness. From these discs chamfered bars of 3 x 4 x 50 mm were machined with final grinding being performed as specified in the EN 843-1 standard. Young's modulus was measured by natural frequency on machined bars of dimension 3 x 4 x 50 mm. The CTE was measured using a Baehr Dil 802 dilatometer between room temperature and 1000°C in a nitrogen/hydrogen atmosphere. The materials were characterised for 4-point flexural strength according to EN843-1, $K_{Ic}$ by SEVNB method in accordance to the recommended practice ESIS P5-00 [3]. After testing specimens were selected for fractography performed according to the recommendations on ceramic fractographical analysis in the ASTM standard C1322-02a and the European standard prEN 843-6.

Tribological characterisations by non-lubricated ball-on-block wear tests in accordance to ASTM G 133 and by wet abrasive tests in accordance to ASTM G 75 were performed.

## 3 RESULTS & DISCUSSION

The results of the fired densities, Young's moduli and $K_{Ic}$ all exhibited a near linear increase with increasing TiN content, presented in Table 1. In addition the CTE also showed a linear increase with TiN content over the temperature range tested as shown in figure 1. The increases in density, Young's modulus and CTE are expected according to the rule of mixtures based on the physical properties of TiN. In accordance to the $K_{Ic}$ results it would be logical that a linear increase in strength may also be expected, assuming a constant average flaw size. However the average strength results show that only the strength of the $Si_3N_4$ + 20 wt.% TiN composite showed any increase over the starting $Si_3N_4$ material. It was observed that the scatter in strength in the composites was lower than in the $Si_3N_4$ and the Weibull modulus was also much higher. Following these strength results a systematic fractographical study was performed on the flexural test specimens.

Table 1: Physical and Mechanical Properties of $Si_3N_4$–TiN composites

| Wt. % TiN Content | Density (g/cm$^3$) | E (GPa) | $K_{Ic}$ (s.d.) (MPa m$^{1/2}$) | Strength (s.d.) (MPa) | Weibull Modulus |
|---|---|---|---|---|---|
| 0 | 3.22 | 303 | 4.26 (± 0.09) | 790 (± 122) | 6.7 |
| 10 | 3.35 | 311 | 4.47 (± 0.03) | 685 (± 52) | 16.0 |
| 20 | 3.48 | 317 | 4.62 (± 0.11) | 884 (± 33) | 27.8 |
| 30 | 3.64 | 330 | 4.71 (± 0.05) | 785 (± 51) | 14.8 |

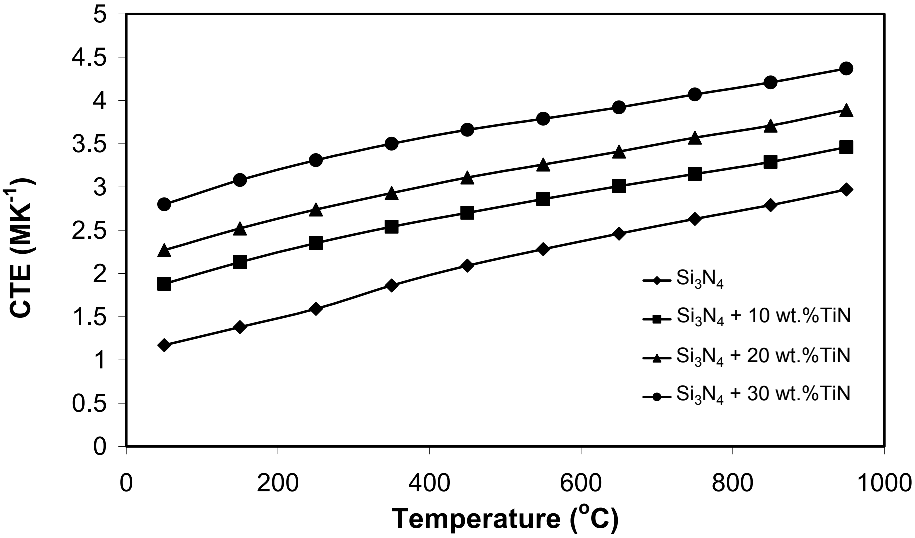


Figure 1: Coefficient of thermal expansion of $Si_3N_4$ and $Si_3N_4$+TiN composites

The specimens were ranked based on their fracture strength. Specimens were selected from each composition with the lowest strengths, typical strengths and highest strengths. Once the fracture origins were obtained by optical and SEM analysis, the size of the defects were measured and the Griffith based equation:

$$\sigma_f = K_{Ic}\sqrt{aY} \tag{1}$$

was used to confirm that the correct feature was identified as the fracture origin. The value *a* is a measure of the flaw size, $\sigma_f$ the failure strength and *Y* the geometrical correction factor which is based on crack geometry and location. For the defects analysed values of $Y$=1.47 for bulk type defects and $Y$=1.59 for semi-elliptical surface defects were used. The importance of use of fracture mechanics to aid correct fracture origin identification was highlighted following a VAMAS round robin [4]. If the $K_{Ic}$ calculated from the measured defect is different by a factor of three from that calculated, e.g. the SEVNB method, then re-verification of the correct facture origin features is required.

In the monolithic $Si_3N_4$ materials the fracture origins were determined to be typical processing defects including localised porosity, agglomerates, inclusions and machining marks. A typical fracture origin is shown in figure 2, of a porous area near the tensile load surface with dimensions of ~50 μm by 25 μm. The failure strength was 878 MPa hence the calculated $K_{Ic}$ from this defect was 4.19 MPa $m^{1/2}$ compared to 4.26 MPa $m^{1/2}$ measured by the SEVNB method.

Optical microscopy of the $Si_3N_4$ + 10 wt.% TiN and $Si_3N_4$+30 wt.% TiN specimens revealed the presence of gold-coloured clusters at the fracture origins. SEM revealed these clusters to be larger clusters of loosely-bonded TiN (white) grains. Figure 3 shows an agglomerate of TiN grains in a $Si_3N_4$ + 30 wt.% TiN specimen that failed at 722 MPa the defect is ~94 μm by 38 μm, the calculated $K_{Ic}$ was 4.56 MPa $m^{1/2}$ compared to a measured value of 4.71 MPa $m^{1/2}$.

The effect of TiN cluster size on strength is clearly observed in two $Si_3N_4$ + 10 wt.% TiN specimens with strengths of 566 MPa and 755 MPa. In the first specimen the fracture origin is shown in figure 4 with dimensions of ~70 µm by 33 µm. In the second specimen shown in figure 5 is ~22 µm by 18 µm and consists of far fewer TiN grains.

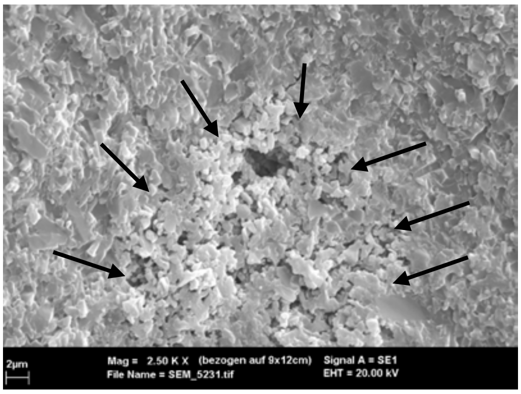


Figure 2: Typical pore type defect in $Si_3N_4$

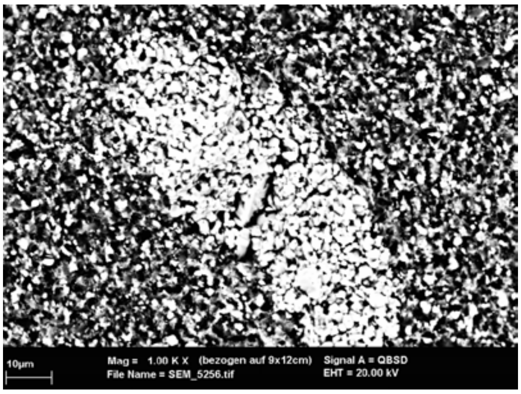


Figure 3: A large agglomerate of TiN grains in a $Si_3N_4$ + 30 wt.% TiN specimen

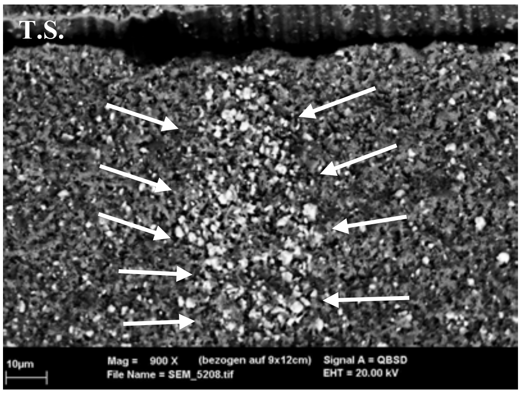


Figure 4: Fracture origin in $Si_3N_4$+ 10 wt. % TiN specimen with $\sigma_f$=566 MPa (T.S.=tensile surfaces)

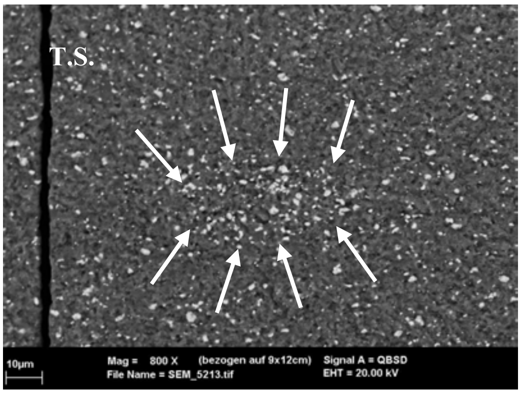


Figure 5: Fracture origin in $Si_3N_4$+ 10 wt.% TiN specimen with $\sigma_f$=755 MPa (T.S.=tensile surfaces)

The $Si_3N_4$ + 20 wt.% TiN composite exhibited the highest average strength as well as the smallest deviation. In optical microscopy examinations no gold-coloured clusters were observed. In addition SEM examination also showed no TiN grain clusters. A typical failure in $Si_3N_4$ + 20 wt.% TiN is shown in figure 6, failure at 892 MPa originated from a machining mark on the tensile surface of dimensions ~60 µm by 10 µm. the $K_{Ic}$ was calculated to be 4.48 MPa $m^{1/2}$ compared to a measure value of 4.62 MPa $m^{1/2}$.

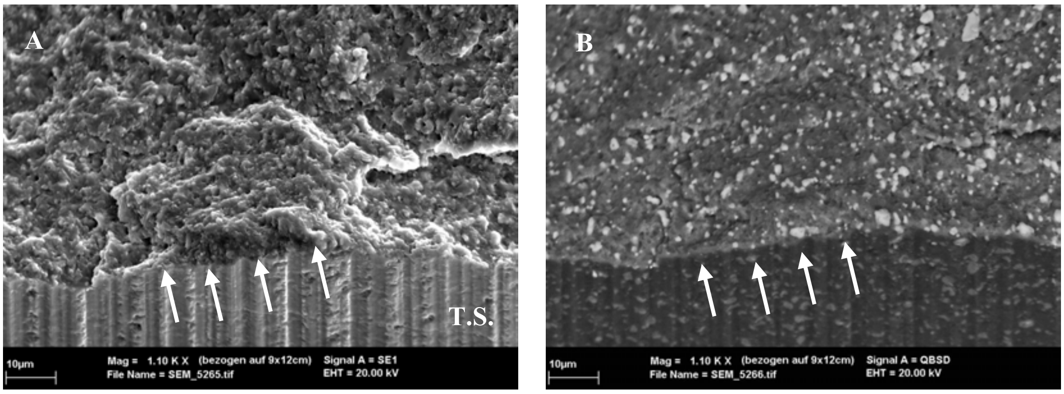


Figure 7: Machining mark (arrowed) on $Si_3N_4$ + 20 wt.% TiN in SE mode A, and in BSE mode B

The good correspondence between the values calculated from the fractographical observations and those measured by the SEVNB method indicate that the true fracture origins were determined. The increase in strength observed in the $Si_3N_4$ + 20 wt.% TiN and the $K_{Ic}$ measurements of the composites indicate that higher strengths can be achieved by elimination and reduction in size of the TiN agglomerate clusters. The agglomerated TiN grains were loosely bonded together, with fissures present between the agglomerate and the $Si_3N_4$ matrix created by the differential shrinkage of the $Si_3N_4$ and TiN phases during hot-pressing.

Following the fractographical analysis, the producer of the composites investigated the wet milling, granulation and sieving processes to reduce and eliminate the TiN based agglomerates. Specimens produced following the process improvement were characterised for flexural strength and the results presented in Table 2. The average strength $Si_3N_4$ + 30 wt.% TiN is now 100 MPa greater than before. It should in theory be possible to obtain further small increase in strength. However it should be noted that the average TiN grain size was ~2 μm in the composites and in the $Si_3N_4$ + 30 wt.% TiN and $Si_3N_4$ + 40 wt.% TiN the TiN grains start to link up during sintering due to their sheer volume. This may effect the toughening mechanisms and failure.

Table 2: Average flexural strength before and after process improvements

| Wt. % TiN Content | Strength Before (s.d.) (MPa) | Strength After (s.d.) (MPa) |
|---|---|---|
| 0 | 790 (± 122) | -- |
| 10 | 685 (± 52) | -- |
| 20 | 884 (± 33) | -- |
| 30 | 785 (± 51) | 888 (±29.6) |
| 40 | -- | 849 (±80.1) |

The aim of the materials development was to produce materials with improved mechanical properties specifically for wear applications. The tribological results showed that the addition of TiN particles improves the wear resistance of $Si_3N_4$ during dry ball-on-block wear testing (Table 3). In the $Si_3N_4$ + 30 wt.% TiN composite the wear resistance is improved three fold compared to that of $Si_3N_4$. However in wet abrasive tests no benefit can be seen by the addition of the TiN taking in to consideration normally scatter in the wear data.

Table 3: Summary of the wear results of the $Si_3N_4$-TiN compositions

| Wt. % TiN Content | Dry SRV-Avg. vol. wear ($mm^3Nm^{-1}$) | Wet Abrasive- Avg. vol./surface wear ($mm^3/mm^2$) |
|---|---|---|
| 0 | $9.9 \times 10^{-5}$ | $5.2 \times 10^{-3}$ |
| 10 | $8.7 \times 10^{-5}$ | $4.5 \times 10^{-3}$ |
| 20 | $4.5 \times 10^{-5}$ | $6.6 \times 10^{-3}$ |
| 30 | $3.3 \times 10^{-5}$ | $6.5 \times 10^{-3}$ |

## 4 CONCLUSIONS

Using a detailed fractographical study combined with microstructural and mechanical characterisation has allowed the identification of a main defect type in $Si_3N_4$-TiN composites. The use of fracture mechanics combined with fractography allows quick and easy confirmation of the critical fracture defects. The elimination by process improvements of the TiN agglomerates and clusters has resulted in higher strength composites with a low deviation in flexural strength and improved $K_{Ic}$. The addition of TiN particles to $Si_3N_4$ was found to considerably improve the dry wear resistance.

## 5 REFERENCES


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