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Micro-, submicro- and nano-Si_3N_4 – SiC composites sintered by the HPHT method

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ABSTRACT

Purpose: The purpose of the presented work is to study the influence of different Si_3N_4 and SiC powders on mechanical properties of Si_3N_4–SiC composites, to obtain a hard and tough engineering material, especially for cutting applications.

Design/methodology/approach: Three kinds of Si_3N_4 – SiC composite, with initial powders of different grain size: micro-, submicro- and nano-structured, were sintered by the HPHT (High-Pressure High-Temperature) method. Several variants were made of each composite, with different Si_3N_4 to SiC phase volume ratios. The influence of grain size of the initial Si_3N_4 and SiC powders on mechanical properties of sintered materials was investigated. Density, Young's modulus, hardness and fracture toughness of composites were measured. Microstructural (SEM) investigations were also conducted for selected samples.

Findings: A strong influence of initial powder size on mechanical properties of Si_3N_4 – SiC composites can be observed. Sintered materials obtained from submicron powders are characterized by better mechanical properties than those obtained from micro- and nanopowders.

Research limitations/implications: The material obtained is characterized by a good combination of hardness and fracture toughness, but further improvement in toughness is possible by the addition of third phase dispersion particles to the Si_3N_4 – SiC system.

Practical implications: A practical aspect of the research carried out is an improvement in mechanical properties of silicon nitride and silicon carbide-based composites. Following additional technical exploitation tests, the materials obtained could be used in cutting tools, various parts of machines and wear components.

Originality/value: The composites obtained have a better combination of mechanical properties than comparable commercial materials.

Keywords: Nanomaterials; Composites; Mechanical properties; HPHT

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MATERIALS

1. Introduction

In recent years, there has been considerable interest in the mechanical properties of ceramic nanocomposites. In application, the most interesting properties of nanocomposites are their strength, fracture toughness, wear, creep and high temperature performance [1, 2, 3].

A number of combinations of reinforcement and matrix have been reported in the literature but most studies have concentrated on SiC reinforcements in Al_2O_3 or Si_3N_4 matrix [1, 2, 4, 5]. Silicon nitride has a favourable combination of properties that include high strength over a broad temperature range, high hardness, moderate thermal conductivity, low coefficient of thermal expansion, moderately high elastic modulus, and relatively high fracture toughness for a ceramic. Silicon nitride ceramics have reached large-scale production for cutting tools, bearings, turbocharger rotors and a variety of custom wear parts. Silicon carbide has many of the same applications as silicon nitride. Most of the silicon carbide materials have very high hardness (harder than alumina and silicon nitride) and thus have superior wear resistance [6, 7, 8, 9]. A major disadvantage of SiC ceramics materials is their low fracture toughness, which usually does not exceed about 3.5 $MPa \cdot m^{1/2}$ [10, 11]

Some papers indicate that ceramic-based nanocomposites present a great opportunity to improve fundamentally the mechanical performance of ceramic materials even at high temperatures [4, 5, 12]. Nanopowders could theoretically be easier to densification in comparison with conventional, microstructured powders. Nanopowders have a large specific surface area of particles and a large surface free energy, which contributes to intensification of the sintering process. On the other hand, in practice, some common problems with densification of nanopowders are known. The large specific surface area of nanograins causes a tendency to absorb a high amount of different gases and impurities. These impurities often contribute to the cracking of sintered nanomaterials. Another difficulty in the consolidation of particulate nanostructured materials is ensuring complete compaction with retaining the nanocrystalline structure and preventing an intensive recrystallization process.

Many different processing methods are applied to nanocomposites. As a starting material for the sintering of Si_3N_4 – SiC composites, either a CVD (Chemical Vapour Deposition) in situ-obtained special Si-C-N composite precursor or a mixture of silicon nitride and silicon carbide powders can be used [1, 2, 4, 13]. For densification of ceramic nanocomposites, free sintering, Hot Pressing (HP), Hot Isostatic Pressing (HIP) or Spark Plasma Sintering can be used [3, 5, 6, 13]. Due to the short sintering duration (usually up to 1-2 minutes), the High-Pressure High-Temperature (HPHT) method is suitable to prevent a recrystallization process and simultaneously limit grain growth [14].

2. Experimental

2.1. Materials preparation

The following micro-, submicro-, and nanopowders were used for the preparation of mixtures: micron powders: Si_3N_4 (alpha>85%), 1-5 μm, AEE, US and SiC, 1.2 μm, AGH, Poland; submicron powders: Si_3N_4 (alpha>90%), grade M11, 0.6 μm, H.C. Starck, Germany and SiC (alpha), 0.1-1 μm, Goodfellow, UK; nanopowders: Si_3N_4 (amorphous), <20 nm, Goodfellow, UK and SiC (beta), <5 nm, France.

The following mixtures were prepared by mixing the appropriate powders in an isopropanol environment using a Fritsch Pulverisette 6 planetary mill (Table 1).

Table 1.
Composition of Si_3N_4 – SiC mixtures

Nanopowders	Submicron powders	Micropowders
100% Si_3N_4	100% Si_3N_4	100% Si_3N_4
Si_3N_4 + 50 vol.% SiC	Si_3N_4 + 50 vol.% SiC	
	Si_3N_4 + 70 vol.% SiC	Si_3N_4 + 70 vol.% SiC

The mixtures, after drying, were preliminarily consolidated into pellets of diameter 15 mm and height 5 mm under pressure of ~200 MPa.

The samples were obtained at high pressure (6 GPa) in the temperature range of 430-2150°C using a Bridgman-type toroidal apparatus. The sintering temperatures were experimentally established for each composite to obtain crack-free samples with the highest values of density and mechanical properties. Duration of the sintering process was 40 s for nanopowders and 60 s for submicron- and micropowders.

The sintered compacts were subsequently ground to remove remains of graphite after the technological process of sintering and to obtain the required quality and surface parallelism for physical and mechanical studies.

2.2. Research methods

Densities of the sintered samples were measured by the hydrostatic method. The uncertainty of the measurements was below 0.02 g/cm^3, which gave a relative error value of below 0.5 % (excluding measurements of small pieces of broken samples, where error was up to 0.1 g/cm^3, due to their insufficient volume and mass).

Young's modulus of the samples obtained by HPHT sintering were measured based on the transmission velocity of ultrasonic waves through the sample, using a Panametrics Epoch III ultrasonic flaw detector. The velocities of transverse and longitudinal waves were determined as a ratio of sample thickness and relevant transition time. The accuracy of calculated Young's modulus was estimated to be below 2 %.

Hardness of selected samples was determined by the Vickers method using a digital Vickers Hardness Tester (FUTURE-TECH FV-700). Five hardness measurements, with indentation loads of 2.94, 9.81 and 98.1 N, were carried out for each sample. Standard deviations of HV values were relatively high but usually no more than 5 % of the average values.

Indentation fracture toughness was calculated from the length of cracks which developed in a Vickers indentation test (with indentation load - 98.1 N) using Niihara's equation (1):

$$(K_{IC}\ \varphi / H\ a^{1/2})\ (H/E\ \varphi)^{2/5} = 0.129\ (c/a)^{-3/2} \quad (1)$$

where: K_{IC} – critical stress intensity factor, φ – constrain factor, H – Vickers hardness, E – Young's modulus, a – half of indent diagonal, c – length of crack.

Microstructural observations were carried out on the densified materials using a JEOL JXA-50A Scanning Electron Microscope equipped with back scattering electron (BSE) imaging.

3. Results

Density and Young's modulus of Si_3N_4 – SiC sintered materials are presented in Figs. 1 and 2. Theoretical density (dashed lines, Fig. 1) and Young's modulus (dashed lines, Fig. 2) of Si_3N_4 – SiC ceramics were calculated by averaging appropriate theoretical values of pure Si_3N_4 and SiC phases.

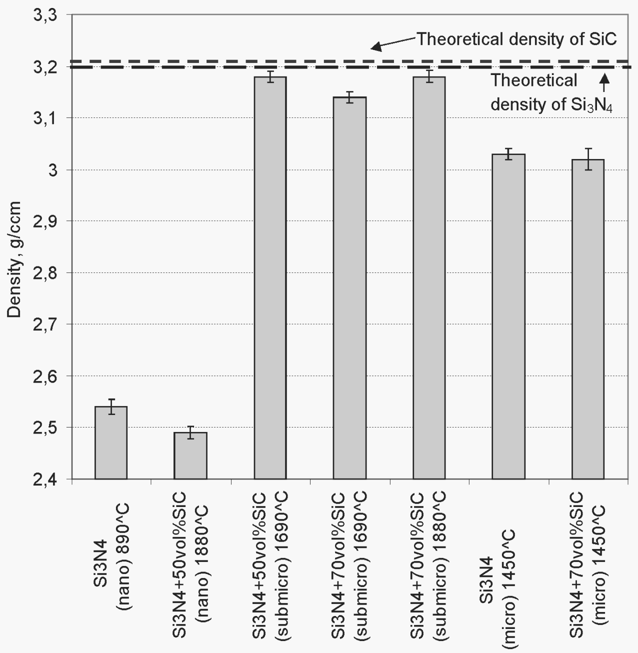

Fig. 1. Density of nano-, submicro-, and micro-Si_3N_4 – SiC composites

Generally, nanocomposites are characterized by the lowest physical-mechanical properties of the three granulometric types of the investigated materials. Densities and Young's modulus values of the best nanostructured samples do not exceed 2.55 g/cm^3 and 135 GPa respectively. In most cases, nano-Si_3N_4–SiC samples are characterized by a lot of cracks. Cracking of such ceramics occurs as a result of the presence in their structure of residual micro- and macro-stresses which overcome the strength of the produced material. The fine powder is characterized by very large specific surface and high gas content in the sample due to the absorption process of the material particles. During heating, as a result of the increase in temperature, the volume of gases increases, which causes cracking or even permanent fragmentation of the sample. In order to prevent the cracking phenomena in the samples, various conditions of the sintering process were tested. Dependent on composition, materials characterized by the highest level of densification and the best mechanical properties were obtained at different temperatures: 890 ^oC for pure Si_3N_4 and 1880 ^oC for Si_3N_4–50 vol.% SiC composite. Unfortunately, some of these samples had cracks as well.

Different kinds of internal cracks, delamination and other defects of microstructure occurred in most of the nanostructured samples. These defects cause a scattering of caustic waves propagated through the material and, in consequence, the impossibility of Young's modulus measurements using ultrasonic probes (nm*, Fig 2).

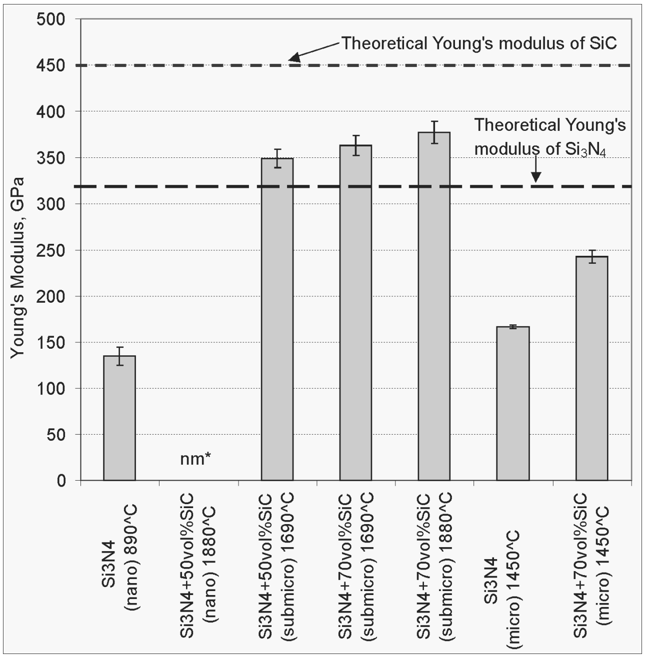

Fig. 2. Young's modulus of nano-, submicro-, and micro-Si_3N_4 – SiC composites; *nm - nonmeasurable by ultrasonic method

Composites without cracks were obtained only from micro- and submicro-structured powders. Only for these composites HV were analyzed and K_{IC} measured.

Composites obtained from submicron powders display the best properties. Density and Young's modulus of the best Si_3N_4–70 vol.% SiC compacts sintered at temperature 1880^{o}C were 3.18 g/cm^3 (Fig. 1) and 377 GPa (Fig. 2) respectively (over 99% and 90% of the theoretical values). This material is also characterized by the highest hardness (HV1 ~3000, Fig. 3) and relatively good fracture toughness (4.9 MPa·m$^{1/2}$). The same material sintered at a lower temperature (1690 ^oC) has slightly lower values of density (3.14 g/cm^3), Young's modulus (363 GPa) and hardness (HV1 2626) but higher fracture toughness (5.6 MPa·m$^{1/2}$). HPHT sintered submicro-Si_3N_4–70 vol.% SiC composites have a better combination of mechanical properties than comparable commercial materials (e.g. StarCeram - an SiC based material produced by H.C. Starck - density - 3.10 g/cm^3, hardness HV1- 2500, fracture toughness - 3.0 MPa·m$^{1/2}$) [15].

Composites obtained from the micro-sized powders have intermediate properties between the nano- and submicro-structured materials. Even though the best micro Si_3N_4–SiC samples are crack free and have fairly good density (>94% of theoretical values) and indentation fracture toughness (4.6 – 4.8 $MPa \cdot m^{1/2}$), their Young's modulus and hardness are much lower than for the submicro-structured samples. The insufficient mechanical properties of micro-sized Si_3N_4–SiC materials can be attributed not only to grain size but also to specific properties of the initial powder resulting from their production method (e.g. shape of the grains, impurities, oxidation etc.). The critical factor in achieving good quality of ceramics is the choice of suitable initial powders for the given method of sintering.

For all investigated samples, independent of their grain size, a strong influence of indentation load on hardness values can be observed. Increasing the indentation load causes a decreasing in hardness values (Fig. 3).

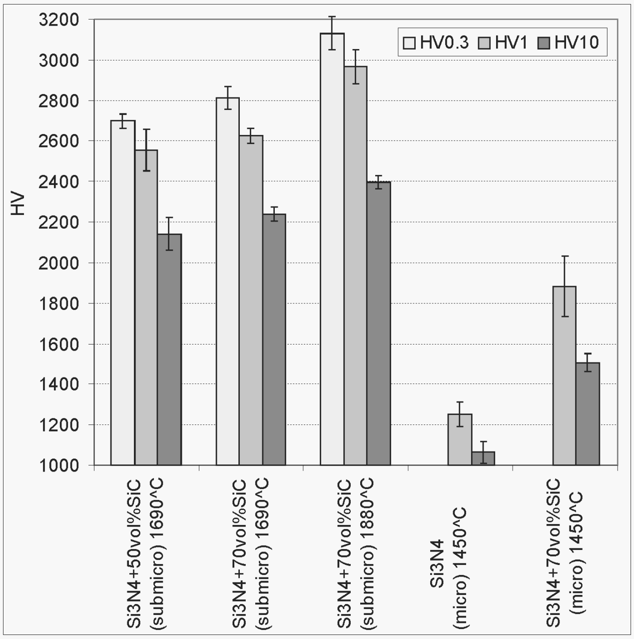

Fig. 3. Vickers hardness (loads: 0.3, 1 and 10 kG) of submicro- and micro-Si_3N_4 – SiC composites

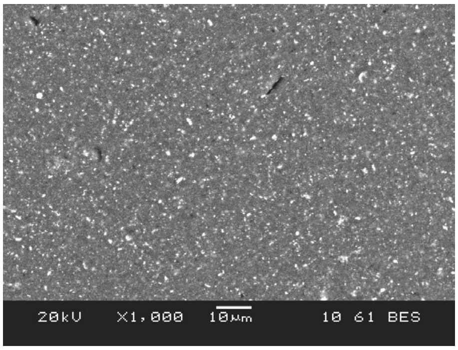

Fig. 4. SEM microstructure of submicro-Si_3N_4 –SiC composite

Submicro-sized Si_3N_4 – SiC sintered materials are characterized by a low level of porosity and a homogenous microstructure with ingredients uniformly distributed (Fig. 4). Micro-sized materials have similar microstructures.

4. Conclusions

The influence of different (nano-, submicro- and micro-structured) initial Si_3N_4 and SiC powders on mechanical properties of Si_3N_4–SiC composites sintered by the HPHT method was investigated.

Nanocomposites are characterized by the lowest physical-mechanical properties of the three granulometric types of the investigated materials. The poor quality of these materials can be attributed mainly to the high gas content in the samples due to the absorption process on nano-particles of initial powders.

Composites obtained from submicron powders display the highest density, Young's modulus, hardness and fracture toughness. HPHT sintered submicro-Si_3N_4–SiC composites have a better combination of mechanical properties than comparable commercial materials.

The investigated properties predispose submicro-structured Si_3N_4–70 vol.% SiC composites to application in cutting tools. Wear tests and cutting tests (intended in the future) will show the range of applications of this material in machining.

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