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Hetero-modulus Nanoparticles Reinforced Corundum Matrix CMC with Extreme Wear and Thermal Shock Resistances

László A. Gömze [1,a] Ludmila N. Gömze [2,b]

[1]Department of Ceramics and Silicate Engineering, University of Miskolc, Hungary

[2] IGREX Engineering Service Ltd., Igrici, Hungary

[a]femgomze@uni-miskolc.hu; [b]igrex2009@yandex.ru

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Abstract:

A novel approach to obtain ceramic matrix composites with extreme high mechanical wear and thermal shock resistance abilities is presented. The developed corundum matrix composites were reinforced with nanoparticles, submicron fibres and whiskers of Si_2ON_2, SiAlON, AlN and Si_3N_4. These kinds of materials have several Young's modulus simultaneously. These new alumina based ceramic matrix composites were obliged to collisions with different metallic bodies having high densities and impact speeds larger than 900 m/s at the moment of the hits. During the experiments in the places of collisions where oxygen was absent new high density „diamond-like" c-Si_3N_4 cubic crystals have developed with spinel structures, where nitrogen atoms were distributed in the centres of the cubes. These new spinel crystals of c-Si_3N_4 in the alumina matrix have extreme high dynamic strength, hardness and wear resistance, like diamond. They were fully resistance to oxygen and thermal shock at the tested temperature of 1200 ^oC.

Introduction

Several kinds of ceramic materials and ceramic matrix composites with submicron and nanoparticles were developed for different industrial and biomedical purposes [1-9] in the last 10-15 years. There were also developed ceramic materials CMC-s with extreme high values of mechanical strength, hardness and wear resistance [10-16]. Some of them are made from hetero-modulus ceramics [12, 14] and have very good resistance to high temperature and thermal shock. The hetero-modulus ceramic materials and CMC-s give us an opportunity to combine ceramic matrix having high Young's modulus (200-400 GPa) with additions of particulate or fibrous phases having significantly higher (500-800 GPa) or lower (10-60 GPa) Young's modulus. The thermal shock resistance of brittle ceramic compounds, such as hard oxides, carbides, nitrides, borides can be developed to a considerable extent by addition of lower modulus particles. These ceramics and CMC-s because of their hetero-modulus material structures have inherent ability to absorb and dissipate the elastic energy and divert the crack propagation. Opposite to hetero-modulus materials the traditional hard metals, oxide, carbide, nitride, boride and silicone ceramics and CMC-s usually have material structures with relatively big crystals with high rigidness and have strong inclination to nick, pitting and rigid fractures [17,18].

The physical and mechanical properties including the mechanical strength, hardness, wear and thermal shock resistances of technical ceramics and CMC-s are very strong dependent both on chemical compositions, crystal structures and the used technological conditions and processes [9, 10, 19, 20, 21]. These technological parameters are the followings:

- The grain sizes and shapes of the used raw material powders and their distribution in the forming instruments before, during and after compacting.
- The volumes, sorts and distributions of mechanical pressures in the ceramic powders during their compacting.

- The level of relaxation of the mechanical residual stresses inside the compacted ceramic items after forming and before sintering.
- The level and time of relaxation of thermo-mechanical stresses developed in ceramic and CMC items during sintering at high temperatures.

The level of recrystallization and residual thermo-mechanical stresses strong depend on firing conditions including firing curves, temperatures and atmospheres [19, 22, 23, 24, 25].

The aims of present contribution are:

- Develop hetero-modulus corundum matrix composite materials with extreme mechanical properties including dynamic strength, wear and thermal shock resistance.
- Show the opportunities of „cold" phase transformation of pre-compacted and pre-sintered α-Si_3N_4 and β-Si_3N_4 into cubic c-Si_3N_4 silicon nitride diamonds of spinel crystalline structures.

Materials and experimental procedures

To produce hetero-modulus corundum matrix composite (CMC) materials and specimens for further examination on material structure, phase transformation and recrystallization well known and relatively not expensive alumina powders of different purity were used. These powders were polluted with quartz, thallium-oxide and metallic aluminium to a small extent. The content of Al_2O_3 was higher than 92% in each case of experiments. The specimens were manufactured by uniaxial pressing method applying pressures from 400 MPa to 600 MPa. The shapes of specimens were cylindrical and quadrangular prism and they were pre-sintered in nitrogen (N_2) atmosphere under special firing curves. Due to phase transformation and recrystallization occurred during pre-sintering, a new hetero-modulus corundum matrix CMC was developed (Fig. 1.), reinforced with submicron and nanoparticles of Si_2ON_2, AlN and α-Si_3N_4

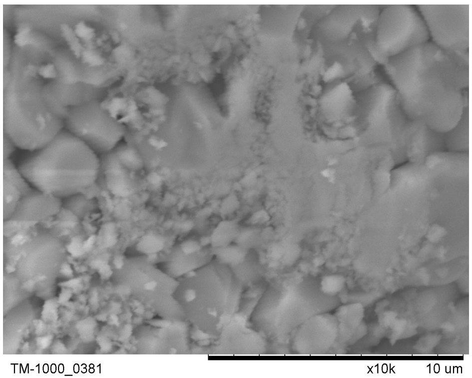

Fig. 1. The material structures of developed hetero-modulus corundum matrix CMC with α-Si_3N_4 particles

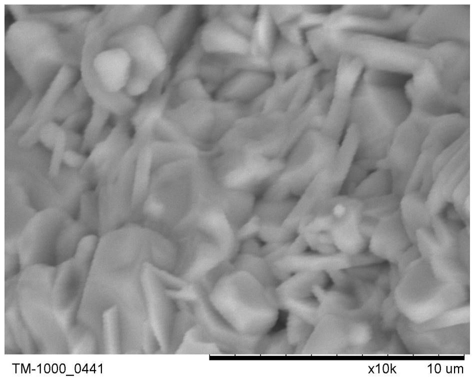

Fig. 2. The material structures of developed hetero-modulus corundum matrix CMC with β-Si_3N_4 particles

There are several methods to develop SiAlON particles and transform α-Si_3N_4 into β-Si_3N_4, but all of them have used sintering temperatures much above 1700 ^oC or hot-pressing at 1850 ^oC under pressure of 23 MPa or more [26-30]. In present work a reactive pre-sintering was used in nitrogen (N_2) atmosphere at temperature from 1350 ^oC to 1550 ^oC. In results of pre-sintering SiAlON and stabilized AlN particles were developed in the corundum matrix and the crystals of α-Si_3N_4 have transformed into β-Si_3N_4 which growth in longitudinal direction prismatic hexagonal rod-like crystals (Fig. 2). These crystals impinge on each other forming an interlock microstructure [31].

To achieve extreme mechanical and thermal properties, hardness, wear and thermal shock resistance of hetero-modulus corundum matrix composites reinforced with Si_2ON_2, SiAlON, AlN_2, α-Si_3N_4 and β-Si_3N_4 a special, high energy dynamic compacting method with high speed flying punches (Fig. 3) was developed and used.

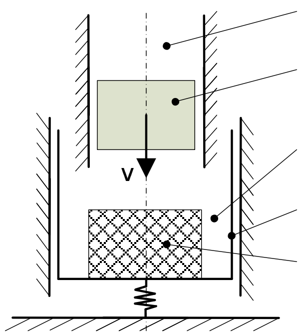

Fig. 3. Principles of dynamic compacting method with high speed flying punches

The flying punches are made from hard metal alloys or from RBSN and HPSN silicon nitride ceramics and flying in vacuum or in nitrogen (N_2) atmosphere of pressure less than 0,1 MPa and have speeds more than 900 m/s.
To examine the thermal shock behaviour of developed hetero-modulus corundum matrix ceramic composites reinforced with different nitrides, including cubic c-Si_3N_4 diamond particles, quenching tests under water were used.

Results and discussion

Improvement of mechanical and thermal properties including dynamic strength [15, 32], hardness [33, 34], wear [12, 35] and thermal shock [14, 36, 37, 38] resistance is very important in development of high performance ceramics and CMC-s. Because of this, several methods were developed to achieve phase transformation in silicon nitride ceramics and obtain Si_3N_4 particles with extreme mechanical properties and dynamic strength [24, 31, 32, 38, 39, 40, 41], but no one of them used flying punches with speeds higher than 900 m/s to generate phase transformation process at „room-temperature". During the hits of flying punches into hetero-modulus corundum matrix composite specimens reinforced with Si_2ON_2, AlN, α-Si_3N_4, SiAlON, and β-Si_3N_4, the kinetic energy of flying punches is engorged (Eq.1) by fractures, heating and phase transformation with recrystallization of material particles in the place and surrounding of the collisions:

$$W_k = W_F + W_H + W_{PT}, \qquad [\text{Nm}]; \qquad (1)$$

where:
W_k – kinetic energy of flying punches [Nm],
W_F – energy engorgement through fractures [Nm],
W_H – energy engorgement through local heating [Nm],
W_{PT} – part of kinetic energy turned to phase transformation and recrystallization of material particles both of flying punches and corundum matrix composite specimens in the place and surrounding of the hits and collisions.

When flying punches have homogeneous density and the specimens are made from hetero-modulus materials like corundum matrix composite reinforced with Si_2ON_2, AlN, α-Si_3N_4 SiAlON, and β-Si_3N_4 particles with several Young's modulus, the part of kinetic energy turned on heating and phase transformation were mathematically determined and described in [18] and [23].

When flying punches have high densities and speeds higher than 900 m/s, a huge volume of kinetic energy is turning to phase transformation, which is accompanied with local temperature over 1000 ^{o}C and mechanical stress larger than (150 – 200) GPa. Due to high pressures and local overheating, phase transformation and recrystallization could be observed both in alumina poly-crystals and α-Si_3N_4 and β-Si_3N_4 nanoparticles of hetero-modulus corundum matrix composites reinforced with different nitrides. The geometrical sizes of alumina poly-crystals had grown considerable (Fig. 4.) and the density of corundum matrix also had increased. At the same time the particles of α-Si_3N_4 and β-Si_3N_4 transformed into diamond-like cubic c-Si_3N_4 of spinel crystalline structure (Fig. 5.).

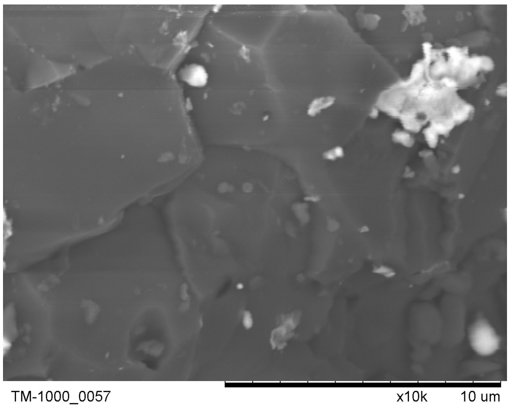

Fig. 4. The material structures of recrystallised alumina poly-crystals

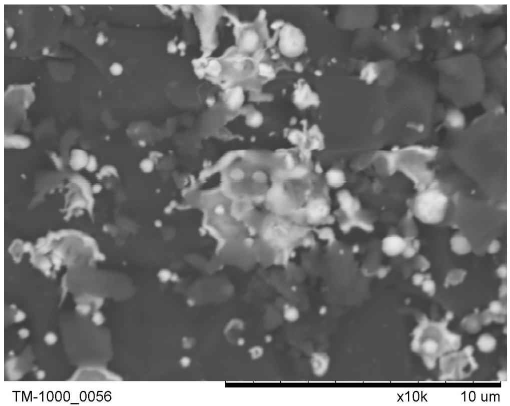

Fig. 5. The material structures of recrystallised c-Si_3N_4 silicon nitride diamonds

Using the new developed high kinetic energy compacting method, both the corundum matrix crystals (Fig.4.) and the formed c-Si_3N_4 spinel silicon nitride diamond crystals (Fig.5.) are polluted with melted particles of high speed metallic flying punches. Disadvantages of metallic and metal alloy flying punches are their damages and mackles on the surfaces of re-compacted specimens (Fig.6.) and their aptitude and inclination to oxidation (Fig. 7.) The metallic particles of high speed flying punches behave as a reducer material and they can take oxygen ions from the contact surface of corundum matrix, decreasing its physical, chemical and mechanical properties. Because of this, the best materials for high speed flying punches with high kinetic energy are HPSN-s, the dense sintered silicon nitrides.

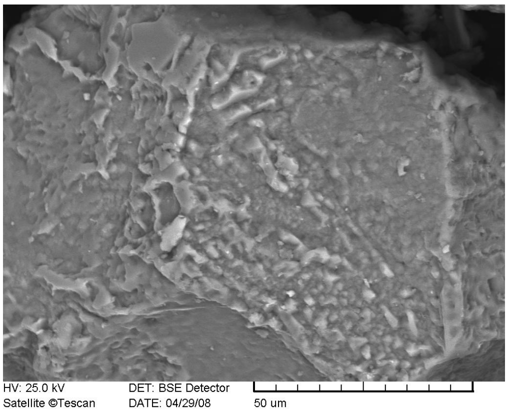

Fig. 6. Mackles of metallic flying punches material on surface of recrystallised CMC specimens

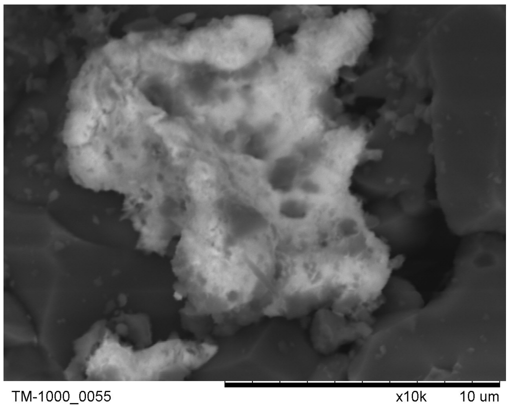

Fig. 7. Mackles and oxidation of metallic flying punches particles on surface of CMC specimens

To examine the thermal shock resistance of developed hetero-modulus corundum matrix composites, reinforced with different silicon nitrides including cubic c-Si_3N_4 diamond particles, quenching tests under water were used. For thermal shock tests the specimens had geometrical forms of disks of diameter 25 mm and thickness 10 mm and were prepared from the following 3 material compositions:

a, Al_2O_3 = 91%, CrO_3 = 1%, ZrO_2 = 1%, CaO = 1%, MgO = 2% and SiO_2 = 4%

b, Al_2O_3 = 97%, MgO = 1%, CrO_3 = 1 %, SiO_2 = 15

c, The developed by us hetero-modulus corundum matrix composite reinforced with silicon nitrides, including c-Si_3N_4 diamond particles.

From each material composition 100 pieces of specimens were made for examination of thermal shock properties. During the tests the specimens were heated up to 1200 ^oC, than dropped into water of 20 °C temperature. The results of samples damages during thermal shock tests are shown on histograms (Fig. 8.). It can be seen from Fig.8. that 40% of specimens from material composition "a" and "b" were cracked or broken but none of 100 pieces of the hetero-modulus ceramic matrix composites reinforced with silicon nitrides, including c-Si_3N_4 diamond particles were damaged after 17 cycles of water quenching test.

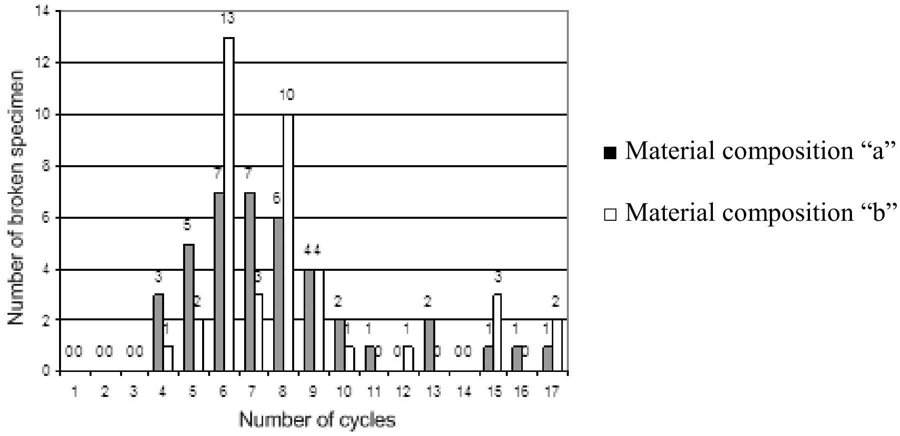

Fig. 8. The results of thermal shock quenching tests under water of 20 °C

The reason is that opposite to traditional powder ceramics and hard metal alloys, there are no remarkable residual mechanical stresses in the hetero-modulus ceramics and CMC-s after forming and sintering, because of their inherent ability to absorb and dissipate the elastic energy developed by mechanical and thermo-mechanical stresses.

Conclusions

Understanding the phenomena in the collisions under high speeds and advantageous of hetero-modulus materials having several Young's modulus simultaneously, new composite material was developed, reinforced with submicron and nanoparticles of AlN, Si_2ON_2, SiAlON and other silicon nitrides. Using the advantageous of high energy dynamic compacting methods with high speed flying punches, at the places and surroundings of hits and collisions new, cubic c-Si_3N_4 silicon nitride diamond particles were developed with spinel crystalline structures.

Transformation of α-Si_3N_4 and β- Si_3N_4 particles into cubic c- Si_3N_4 silicon nitride diamond spinel crystals under high energy collisions with high speed flying punches together with submicron and nanoparticles of AlN and SiAlON give to the new developed hetero-modulus corundum matrix composites not only excellent mechanical strength and surface hardness, but outstanding thermal stability, wear and thermal shock resistance at temperature drops higher than 1000 °C.

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