

Alumina-based hetero-modulus ceramic composites with extreme dynamic strength – phase transformation of Si_3N_4 during high speed collisions with metallic bodies

LÁSZLÓ A. GÖMZE ▪ Department of Ceramics and Silicate Engineering, University of Miskolc ▪ femgomze@uni-miskolc.hu

LUDMILA N. GÖMZE ▪ IGREX Engineering Service Ltd. ▪ igrex@freemail.hu

Till today several kinds of ceramics and ceramic matrix composites are developed for extreme environmental conditions. Most of these ceramics have microstructures with relatively „big” crystals, having high rigidness and strong inclination to nick, pitting and rigid fractures, so they are not usable for collision with metallic or other bodies under high speeds like 800 m/sec or more. On the basis of several years experiments in development and testing of ceramic materials and corundum matrix composites the authors successfully developed new alumina-matrix composite materials reinforced with Si_2ON_2 , SiAlON, AlN and Si_3N_4 . These new alumina based ceramic matrix composites were tested under collisions with different metallic bodies having high densities and speeds higher than 800 m/sec. During the collisions the kinetic energy of flying metallic objects distributing to fracture energies, heatings and recrystallizations both of ceramic and metallic bodies. In the centres of collisions, where oxygen was absent, the authors have found new, high density “diamond-like Si_3N_4 ” materials with cubic crystals, where nitrogen atoms distributed in the centres of the cubes. These new crystal structures of Si_3N_4 in the alumina matrix have extreme dynamic strength and hardness, like diamond. Having surplus of oxygen in the centres of collisions this new “diamond-like Si_3N_4 ” was not observed, when a very strong oxydation of metallic bodies was taken place.

Using the energy conception of collision, the authors mathematically described the energy engorgements of destruction of ceramic materials and heating of participating bodies as well as energy engorgement used for the phase transformations of ceramic and metallic particles during their collision.

Keywords: hetero-modulus, Young’s modulus, ceramics, Si_3N_4 diamond, CMC, alumina, collision, dynamic strength, energy engorgement, nano-particles, hardness.

1. Introduction

In the last 15–20 years the engineers and experts working in ceramic manufacturing plants and scientists working in laboratories of universities and research institutions have been engaged into development of more efficiency ceramic materials and items for different industrial purposes [1, 2, 3, 4]. Till today several kinds of ceramic materials and ceramic matrix composites are developed with high values of mechanical strength and hardness [5, 6, 7, 8]. Most of these ceramics or ceramic matrix composites have materialstructures with relatively „big” crystals, having high rigidness and strong inclination to nick, pitting and rigid fractures, so they do not have the required dynamic strength, and they are not suitable for collision with other materials and bodies under high speeds. Because of these, most of ceramics and CMC-s cannot be used for collision with metallic bodies having high densities and speeds higher than 800 m/sec.

The mechanical properties including the dynamic strength of high performance technical ceramics and CMC-s very strong depend not only on chemical structures and components, but from the technological parameters and processes as well [9, 10, 11, 12]. These technological parameters, which are influencing very strong on mechanical behaviour and dynamic strength of alumina matrix ceramic composites, are the followings:

- the grain size and shapes of the used raw material powders and their distribution in the forming instruments before, during and after compacting;
- the values and distributions of mechanical forming pressures in the ceramic powders during their compacting [13];
- the level of relaxation of the inside pressure in the compacted ceramic items after forming and sintering;
- the firing temperatures, firing curves and atmospheres of their syntering [14].

2. Materials and theoretical procedures

Applying the well-known and relatively not expensive raw materials of alumina powders and using uni-axial pressing and creating a special forming pressure distribution during the compacting and applying a special sintering atmosphere and technology, a new sort of hetero-modulus corundum matrix composite materials with extreme mechanical properties was developed. This new sort of corundum matrix composite materials, reinforced with Si_3N_4 , Si_2ON_2 , SiAlON and AlN

László A. Gömze

is head of Department of Ceramics and Silicate Engineering in the University of Miskolc since 1999. He has got scientific degree „Candidate of Technical and Engineering Sciences” at Moscow University M. I. S. I. in 1985, and has a wide range of experiments both in engineering and research works at different companies and in teaching of students at universities. Finishing the Civil Engineering University of Moscow (Russia) in 1973, L. A. Gömze started his working activity as structural engineering at the design department in Hungarian firm Building Ceramics (Épületkerámia) in Budapest. In 1986 he was already the managing director of the famous Hungarian porcelain manufactory HOLLÓHÁZA. Leaving Hollóháza in 1990 he used to work as associated professor at University of Miskolc. Laszlo A. Gömze is member of several Hungarian and international organization in fields of ceramics, material sciences and chemistry. He is member of „Kerpely Antal Doctoral School” of material sciences and technologies. Since 1996 he has successfully supervised several PhD students in fields of ceramics and ceramic matrix composites.

Ludmila N. Gömze

is the managing director of engineering service firm IGREX Ltd. Finishing the Civil Engineering University of Moscow (Russia) in 1974 she started her working activity as structural engineer at Hungarian design institution VIZITERV in Budapest. Further she continued her job as designer engineer at firm KEVITERV in city Miskolc. In her working experiments she met with the problems of productions and technologies of ceramic items at the porcelain manufactory HOLLÓHÁZA in 1987. Since then she has a wide range experiments in examination, research and development of new material compositions and technologies both of traditional and high-tech structural ceramics as well as of ceramic matrix composites. The research works of Ludmilla N. Gömze are presented in several research reports, conference publications and 5 scientific articles in different German and Hungarian journals.

particles of sub-microne and nanosizes has not only excellent compressive and bending strength and high surface hardness, but excellent dynamic strength as well, during collisions with metallic bodies of high density. They have especially good dynamic strength during collisions, when the speeds are higher than 800 m/sec. The typical forms of microstructures of these new hetero-modulus alumina matrix ceramic composites are shown in Fig. 1. On these microstructure pictures the submicrone and nano-size grains and whiskers of Si_2ON_2 , SiAlON , Si_3N_4 and AlN can be seen, which are distributed roughly uniform between the polycrystals of alumina.

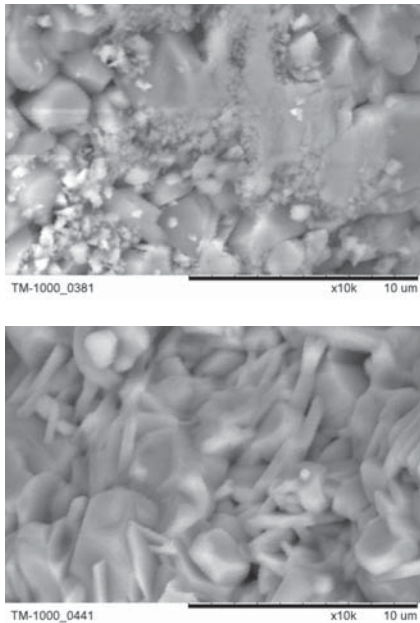


Fig. 1. The materialstructure of the developed corundum matrix composite
1. ábra A kifejlesztett korund-mátrixú kompozit anyagszerkezete

In Fig. 2. the typical destructions of high purity alumina ceramic items are shown after collisions with high density metallic bodies, flying with speeds higher than 800 m/sec.

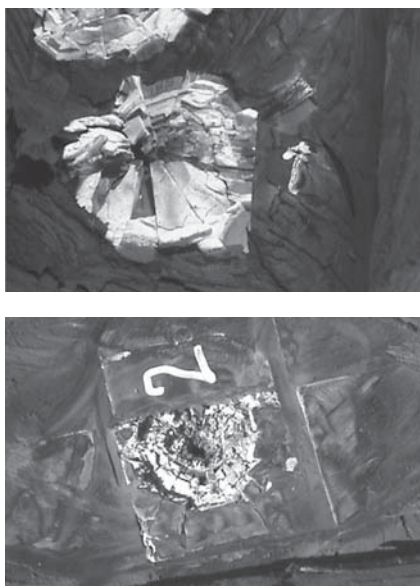


Fig. 2. Typical destruction of ceramic items during high speed collisions
2. ábra Kerámia lapkák tipikus roncsolódása a nagy sebességű ütközés során

These kinds of destructions and cracks show that during the collisions the kinetic energy of flying objects is engorged by fractures through pressure stress and shear stress, as well as heating and phase transformation with recrystallization of material particles in the place and surrounding of the collisions. This phenomena can be described by Eq. 1.

$$W_K = W_p + W_s + W_H; \text{ [Nm]} \quad (1)$$

where:

W_K – kinetic energy of flying object, [Nm];

W_p – fracture energy engorgement through pressure stress, [Nm];

W_s – fracture energy engorgement through shear stress, [Nm];

W_H – energy engorgement through heating and recrystallization of flying object particles and alumina-based ceramic materials in place and surrounding of the collision, [Nm].

The kinetic energy of flying objects very strong depends on their density and its homogeneity. The energy conception of collision was presented on XIth Khariton's Reading [15] and described in details in proceedings of this International Conference [16].

When flying (metallic) object has homogeneous density during high speed collision the energy engorgement by destruction of ceramic bodies having only one Young's modulus can be described by Eq. 2.

$$\frac{u^2}{2} \rho \cdot V = \frac{R_p^2}{2E} \cdot A_1 \cdot l_1 + \frac{R_s^2 \cdot (v+1)}{E \cdot v} \cdot A_2 \cdot l_2 + W_H; \text{ [Nm]} \quad (2)$$

where:

ν_1 – the Poisson ratio;

ρ – density of the flying object, [kg/m³];

A_1 and A_2 – surfaces of fractures, [m²];

E – Young's modulus of ceramic material, [N/m²];

l_1 and l_2 – deep and length of fractures, [m];

R_p and R_s – the pressure and shear strength of ceramic plates or tiles, [N/m²];

u – speed of flying object at the moment of collision, [m/s];

V – volume of the flying object, [m³].

In virtue of Fig. 1. it is easy to understand the submicrone grains, whiskers and nano-particles containing nitrogens have different values of Young's modulus comparing with the alumina matrix and themselves. These kinds of materialstructures have a composition of several Young's modulus, multiple mechanical properties and named hetero-modulus materials [15, 16, 17, 18, 19]. The dynamic strengths of these developed new hetero-modulus ceramics were examined under collisions with high density metallic bodies flying with speeds higher than 800 m/sec. As it is shown in Fig. 1., alumina-based ceramic composites developed by us have submicrone and nano-size grains and whiskers of Si_2ON_2 , SiAlON , AlN and Si_3N_4 , which have different Young's modulus. The energy engorgement of these hetero-modulus ceramic bodies during high speed collisions

strong depends both on values of Young's modulus of hetero-modulus ceramics and on inhomogeneity of densities of flying objects. When the flying objects are built-up from materials of inhomogeneous densities and ceramics have several Young's modulus, the energy engorgement of these hetero-modulus ceramics can be described by the followings:

$$\frac{u^2}{2} \sum_{i=1}^n \rho_i \cdot V_i = \sum_{j=1}^N \frac{R_{pj}^2}{2E_j} \cdot A_{1j} \cdot l_{1j} + \sum_{j=1}^N \frac{R_{sj}^2 \cdot (v_j + 1)}{E_j \cdot v_j} \cdot A_{2j} \cdot l_{2j} + W_H; \text{ [Nm]} \quad (3)$$

where:

ρ_i – density of the „i-th” component of flying object, [kg/m³];

v_j – the Poisson ratio of „j-th” Young's modulus component of ceramic body;

A_{1j} and A_{2j} – surface of fractures of „j-th” Young's modulus component of ceramic body, [m²];

E_j – the Young's modulus of the „j-th” component of ceramic body, [N/m²];

$i = 1, 2, \dots, n$ – the numbers of different density components of flying object;

$j = 1, 2, \dots, N$ – the number of different Young's modulus components of ceramic body;

l_{1j} and l_{2j} – deep and length of fractures of „j-th” Young's modulus component of ceramic body, [m];

R_{pj} and R_{sj} – the pressure and shear strength of „j-th” Young's modulus component of ceramic body, [N/m²];

u – speed of flying object at the place and moment of collision, [m/s];

V_i – volume of „i-th” density component of flying object, [m³].

The “thermic part” of collision energy, which means the energy engorgement through heating, phase transformation and recrystallization of flying object particles and alumina-based CMC materials in place and surrounding of the collision can be described by Eq. 4.

$$W_H = W_{HS} + W_{RC} + W_{RM}; \text{ [Nm]} \quad (4)$$

where:

W_H – energy engorgement through heating, [Nm];

W_{HS} : – energy engorgement through heat transfer and heating of materials in and surrounding of the collision and fall, [Nm];

W_{RC} – energy engorgement through recrystallization of ceramic particles in and surrounding of the collision and fall, [Nm];

W_{RM} – energy engorgement through melting, spraying and recrystallization of the falling metallic body, [Nm].

Measuring the temperatures, the deeps and lengths of destructions and cracks of ceramic items in the places and surroundings of collisions, from Eq. 3. and Eq. 4. the part of kinetic energy, turned into phase transformation and recrystallization of ceramic particles can be mathematically solved and described by Eq. 5.

$$W_{RC} = \frac{u^2}{2} \sum_{i=1}^n \rho_i V_i \left(\sum_{j=1}^N \frac{R_{pj}^2}{2E_j} \cdot A_{1j} \cdot l_{1j} + \sum_{j=1}^N \frac{R_{sj}^2 (v_j + 1)}{E_j v_j} \cdot A_{2j} \cdot l_{2j} \right) (W_{HS} + W_{RM}) \text{ [Nm]} \quad (5)$$

If the flying metallic objects have high densities and speeds higher than 800 m/sec, a huge volume of energy is turning to phase transformation, which is in hand with temperature over 1000 °C and pressure stress higher than 150–200 GPa. Because of these, phase transformations and recrystallizations can be observed both in alumina polycrystals and in the Si₂ON₂, SiAlON, AlN and Si₃N₄ submicrone and nano-sized particles and whiskers.

3. Results and discussion

These new corundum matrix composite materials, reinforced with Si₂ON₂, SiAlON, Si₃N₄ and AlN particles and whiskers of sub-microne and nano-sizes have not only excellent compressive and bending strengths, but extreme dynamic strength, as well. Typical destructions of material structures of these new alumina matrix hetero-modulus ceramic composite materials are shown in Fig. 3.

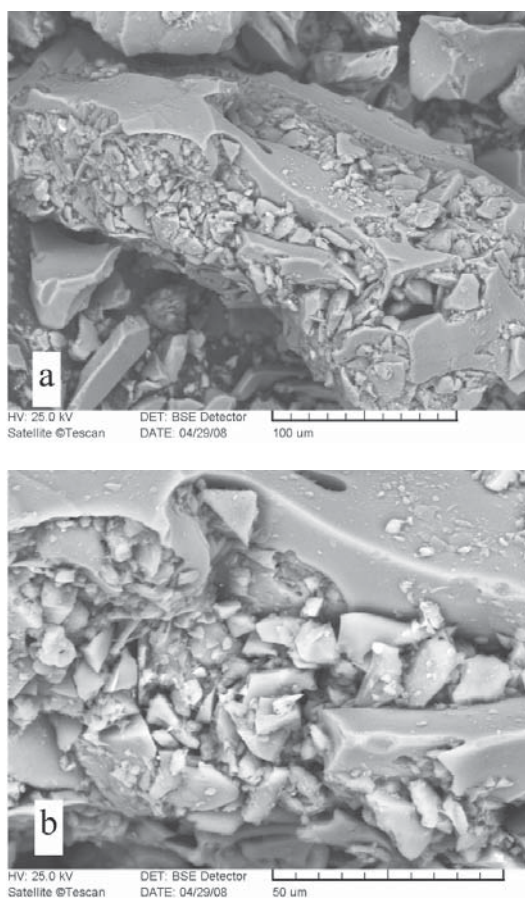


Fig. 3. Destruction of ceramic structures under collision with metallic bodies having speeds about 950 m/sec

3. ábra A kerámia anyagszerkezetének roncsolódása a 950 m/sec körüli sebességgel történő ütközés során

As it can be seen in these SEM pictures during collision with high density metallic bodies flying with speeds about 850–950 m/sec, the directions of destructions of the ceramic microstructure follow the directions of the hits of flying metallic objects. Fig. 3a. shows how some “large” particles destroyed and moved a certain distance together with hit metallic objects.

Fig. 3b. shows how the surface of the hetero-modulus ceramic body can be melted and transformed into amorphous substance at the place and just near of the hits and collisions.

Having surplus of oxygen in places of collisions a very strong oxidation of the falling metallic bodies can be observed, as it is shown in Fig. 4. The energy turned into phase transformation and recrystallization of alumina-based hetero-modulus ceramics is described by Eq. 5. Measuring the depths and lengths of destructions and cracks of ceramic items as well as their temperatures in the places and surroundings of collisions, and substitute them into Eq. 5, it is easy to find the energy, turned into phase transformation and recrystallization of hetero-modulus ceramic materials themselves.

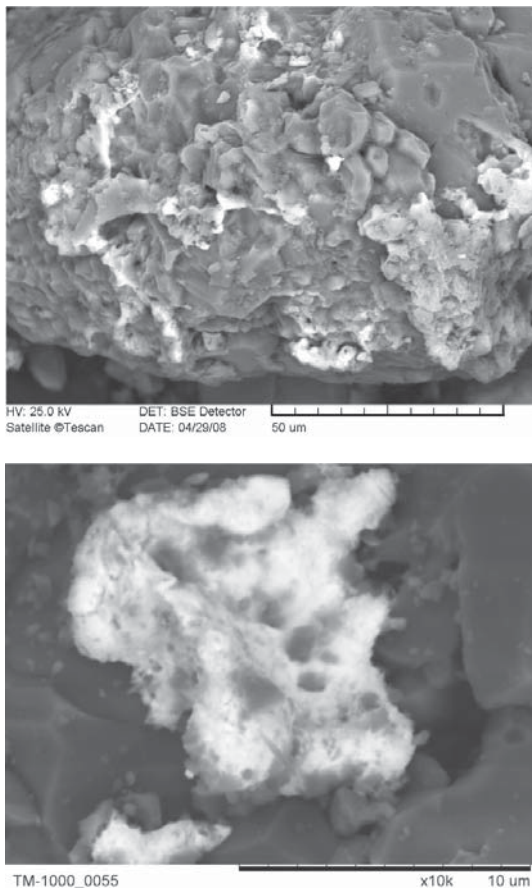


Fig. 4. Typical oxidations of falling metallic bodies, having surplus of oxygen in places of collisions

4. ábra A becsapódó fém test felületének oxidálódása szabad oxigén jelenlétékor az ütközés helyén

During the high speed collisions with high density metallic bodies a strong recrystallization process in the material structures can be observed. The typical recrystallized material structures of the new developed corundum matrix composites, reinforced with submicron and nano-size grains and whiskers of Si_2ON_2 , SiAlON , Si_3N_4 and AlN are shown in Fig. 5., after high speed collisions. When there is no oxygen in the places of collisions and the falling metallic bodies with high density have speeds higher than 800 m/sec, the particles of Si_3N_4 can turn into cubic crystalline structure with nitrogen atoms in the centres of each cubics. These Si_3N_4 particles with

new cubic crystalline structures have high density and extreme high hardness and mechanical strength equivalent to *diamond*. When there was no oxygen at the places of collisions these new “diamond-like Si_3N_4 ” particles were obtained because of the huge volume of collision energy, and followed it very strong recrystallization process. When we had surplus of oxygen in the place of collision, these new “diamond-like Si_3N_4 ” particles were not observed. In these cases strong crystal growth phenomena were taken place as it is shown in Fig. 5b.

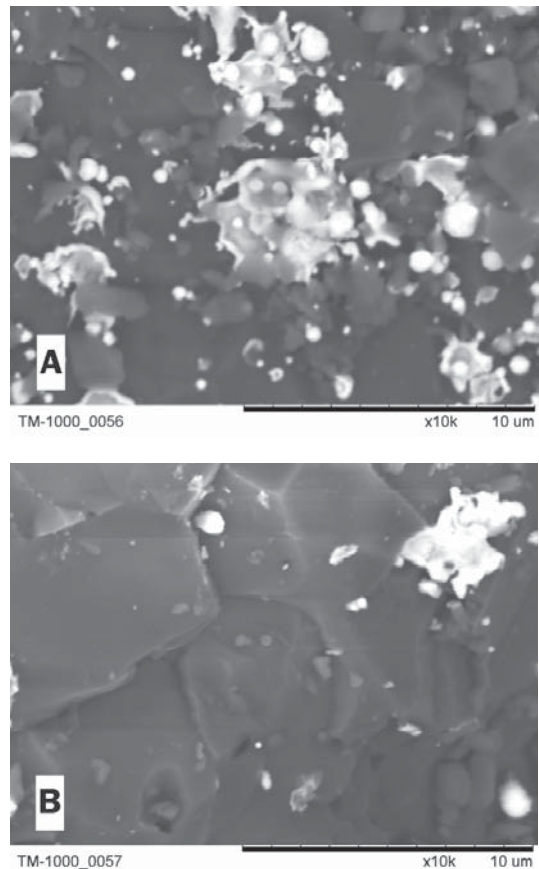


Fig. 5. The recrystallized microstructures of alumina-based ceramic items after collision

5. ábra Az új alumínium-oxid mátrixú kerámia mikroszerkezete nagy sebességű fém-becsapódás után

After the high speed collisions with metallic bodies these new crystals of alumina-based hetero-modulus ceramics, both with recrystallized “diamond-like Si_3N_4 ” (Fig. 5a.) and large alumina crystals (Fig. 5b.) were polluted by sprayed liquid metal drops on their surfaces. These Si_3N_4 ceramic particles with cubic crystalline structures with nitrogen atoms in centres of each cubic, arise in places and surroundings of collisions without oxygen, have excellent mechanical properties and hardness like diamond.

4. Conclusions

Understanding the phenomena in the collisions under high speeds and advantageous of hetero-modulus ceramic materials having several Young's modulus, some new, alumina-based ceramic matrix composites were developed, reinforced with

submicron and nanoparticles of $\text{Si}_2\text{O}_3\text{N}_2$, SiAlON , Si_3N_4 and AlN . These developed new hetero-modulus alumina-based ceramic matrix composites are well-resistant to collisions against metallic objects, flying with speeds between 850–950 m/sec. During the collisions the kinetic energy of flying metallic objects are distributing to energies of fractures, heatings and recrystallizations both of ceramic and metallic bodies participated in the collisions process.

During the high speed collisions with high density flying metallic bodies, in the alumina-based ceramics and CMC-s a strong in-situ crystal growth process can be obtained when we have surplus of oxygen in the places of collisions. This phenomena can be the reason of a rigid fracture of the ceramic items and CMC-s during the next collision with any kind of flying objects.

When there is no oxygen in the places and moments of collisions in the alumina-based ceramic composites reinforced with $\text{Si}_2\text{O}_3\text{N}_2$, SiAlON , Si_3N_4 and AlN , a new, "diamond-like Si_3N_4 " can be developed, having cubic crystals with nitrogen atoms in centres of cubes. These new, "diamond-like Si_3N_4 " ceramic particles have excellent mechanical strength and hardness like diamond.

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Extrém dinamikai szilárdságú alumínium-oxid alapú hetero-modulusú kerámia kompozitok – a Si_3N_4 fázisátalakulása nagy sebességű fém testekkel történő ütközés során

A gyártók és a kutatók napjainkig már számos különleges tulajdonságokkal rendelkező kerámiát és kerámia kompozitot kifejlesztettek. Ezeknek az anyagoknak a többsége ugyanakkor a relatíve nagy, durva szemcsékből álló kristályszerkezet miatt dinamikus igénybevételek esetén hajlamosak a repedésre és a rideg-törsésre; ezért alkalmatlanok a 800 m/sec vagy annál magasabb sebességű fém és egyéb kemény tárgyakkal történő ütköztetésre. A kerámia anyagok és kompozitok kutatásában, fejlesztésében és vizsgálatában megszerzett többéves tapasztalat alapján a szerzőknek sikerült $\text{Si}_2\text{O}_3\text{N}_2$, SiAlON , AlN és Si_3N_4 részecske erősítéssel olyan új alumínium-oxid mátrixú, egyidejűleg több Young-modulussal bíró "hetero-modulusú" kompozit anyagokat kifejleszteni, amelyek kiváló mechanikai tulajdonságokkal rendelkeznek. Ezeknek az új kompozit anyagoknak a dinamikai szilárdságát különböző, nagy test-sűrűségű, 800 m/sec-nál nagyobb sebességgel repülő fém tárgyakkal történő ütköztetéssel vizsgálták. Az ütközés során a repülő fém tárgyak mozgási energiáját az ütközésben résztvevő kerámia és fém testek roncsolódása, felmelegedése és átkristályosodása nyeli el. A szerzők úgy találták, hogy a nagy sebességű ütközés hatására az új kompozit anyagot alkotó valamennyi komponensnél jelentős fázisátalakulás figyelhető meg. Ugyanakkor oxigén-hiányos környezetben az ütközés epicentrumában és annak környezetében a szilícium-nitrid kocka-rácsú „ Si_3N_4 gyémánttá” alakul át, nitrogén atomokkal a kocka-rácsok közepén. Ez az új „ Si_3N_4 gyémánt” adja a kifejlesztett új, alumínium-oxid mátrixú kerámia kompozit rendkívüli nagy dinamikai szilárdságát és keménységét. Neki köszönhető, hogy a kifejlesztett új, „hetero-modulusú” kerámia kompozit viszonylag kis behatolási mélységnél képes megállítani és „ledarálni” az olyan nagy keménységű anyagokat is, mint a wolfram-karbid.

Oxigén felesleg jelenléte esetén ilyen új köbös „ Si_3N_4 gyémánt” szemcséket nem sikerült megfigyelni, miközben az ütközésben résztvevő fémek erősen megolvadtak és eloxidálódtak.

A szerzőknek sikerült matematikailag leírni azt is, hogy ütközés során a „becsapódó” fém tárgy mozgási energiájából mennyi *nyelődik el* a kerámia test roncsolódása, illetve az ütközésben résztvevő kerámia és fém test felmelegedése és fázisátalakulása által.