Structure and properties of the ceramics based on quasicrystal powders processed by plasma coating method

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Abstract. Homogeneous incorporation of a small amount of binding material or modifying agent in the batch consisting of micron size particles is a problem of a composite material production process. In this work the problem is solved by deposition of a thin coating consisting of binding material on the initial powder particles by means of high-rate magnetron sputtering. The confinement of dusty particles in plasma was used in fine powder processing procedure. Composite powders based on the Al-Cu-Fe quasicrystalline particles with nickel coating were obtained. Their investigation showed that the method provides uniform incorporation of small quantities of additives (at concentration of about 3 wt.%) to fine powders. The powders were pressed at room temperature under quasi-hydrostatic conditions at high pressures. After pressing the samples were sintered in hydrogen at normal pressure. Structure and mechanical properties of the sintered samples were studied. The conditions of sintering the composite powder, which provide producing compacts with improved performance data, were established.

1. Introduction
The best combination of the structural components properties, such as strength, ductility, wear resistance, friction coefficient, may be achieved in the composition materials (CM). They find industrial application in the special conditions of high mechanical and thermal loads as material for cutting tools, turbine blades, nuclear fuel, nuclear power plant control rods, high-temperature crucibles, etc. Among the CMs the metal matrix ones armed with the ceramic fillers correspond to extremal operating conditions. The methods of metal matrix CM manufacture base on blending of ceramic powder with metallic one or on infiltration of liquid metal in the porous ceramic blank. In addition, the methods of metal-ceramic CM manufacture exist, which base on
the metal deposition onto particles of ceramic powder or onto fibre carrier and do not include the stage of obtaining the metal matrix [1].

A distinctive feature of quasicrystals is the unique combination of properties including low friction coefficient, high wear resistance, high corrosion resistance, and low adhesion [2]. Most of these properties are highly demanded in modern technologies. However, direct practical application of the quasicrystalline compounds is hindered, in part by their high brittleness [3]. The task of creating a composite material that would retain a low friction coefficient inherent in quasicrystals, while significantly increasing the plasticity, can be solved by introducing a binder into a quasicrystalline powder for the subsequent compaction.

However, the presence of too large amount of the metal binder in ceramics has rather a negative effect upon the thermostability in the process of fabrication and use of the final product [4]. The less the size of inclusions in compacts, the higher the thermostability of the material is. It should be noted that the larger the size of sintered grains in a compact, the higher the surface roughness and less the accuracy of the material processing with the instrument manufactured from it. In case of preliminary blending of reagents the homogeneous distribution of modifying additive fails to be achieved in the sintered charge when the additive concentration is decreased down to less than 5 vol. %, especially for the case the size of sintered particles is less than 5 \( \mu m \) [5].

Deposition of thin layers of the binder upon micron-sized particles with the binder concentration of 2–6 wt. % in the charge can become a perspective approach for production of thermally stable fine-grain compacts [6]. Vapor deposition of metals on the particles not only allows controlling concentration of the binder, but may provide the uniform distribution of the latter in the sintered material. In the case the particles are micron sized, application of the dusty plasma in the vapor deposition methods [7, 8] can be useful. The particles injected in plasma acquire large electric charges, negative in most cases [9]. The like charges prevent from the formation of agglomerates in the wide range of experimental conditions, where the polarization effects are negligible [10]. The cloud of the dispersed particles is confined by electric field in plasma in the regions of larger potential. Such confinement of dispersed particles in the plasma was used at processes of coating the particles by means of magnetron sputtering to produce diamond based composites [11, 12]. The objectives of the present work were as follows: to obtain the uniform coating on the micron sized Al-Cu-Fe quasicrystalline particles in the dusty plasma and, using the obtained disperse composition material as a charge, to produce the bulk composites that contain the additive at a small concentration.

2. Coating method
A scheme of the coating process is given in figure 1. The cloud of particles 1 was formed inside the reactor mounted in the vacuum chamber. To obtain the coating, the levitated particles were exposed to the atomic beam 2 from the magnetron sputter 3, placed in the chamber near the reactor 4.

The mechanical shocks of the metallic reactor shell 4 at the frequency of 50 Hz and amplitude of 1.5 mm provided the persistent injection of the particles of the powder from the disperser 5 into the region where the RF plasma dust cloud was formed. The RF discharge in argon gas was sustained in this region. The grid 6 was the driven RF electrode and the side and top walls of the reactor shell were the cold electrode. The dispersed particles that were injected into the RF plasma 4 confined here due to its electrical charging and the effect of the electric field existing at the plasma boundaries. Metal atoms from magnetron sputter were injected into the vibrating reactor through the metallic grid mounted in the reactor sidewall hole 7.

To produce the quasicrystal-based ceramics we used the Al\(_{65}\)Cu\(_{22}\)Fe\(_{13}\) quasicrystal powder with the size of particles in the range of 0.5–20 \( \mu m \). To remove the adsorbed gas species the reactor containing the powder was heated up to 200\(^\circ\)C and simultaneously pumped out for
15 min at the preliminary stage of experiment. Sputtering of the nickel target was performed under the working gas pressure of 0.4 Pa at the flow rate of 20 sccm. The surface area of a powder batch treated in a run was equal to some square meters. To achieve the appropriate mean sputtering rate we used powerful DC magnetron sputter with direct cooling of the target by running water. The power of the magnetron sputter discharge was 1 kW. The ion current density averaged by the sputtered track area was of 0.1 A/cm². The duration of the deposition process was varied from 40 to 90 minutes. After the process finished the disperse composition material (DCM) consisting of the coated particles was retrieved from the reactor at ambient atmosphere conditions.

3. Method for producing compacts
The quasicrystal-based DCM batches were pressed at room temperature under quasi-hydrostatic conditions at pressures of 8 GPa. After pressing the samples were sintered in hydrogen at normal pressure at flow rate of 10 sccm. The sintering temperature and time were varied in the ranges 445–785°C and 15–60 min, correspondingly. The similar procedures were applied to the batches of the initial quasicrystal powders to compare their properties to the composite ones.

4. Methods of testing sample structure, composition and physical-mechanical properties
The microstructure of the compacts was investigated with SEM. The density of samples was determined by the pycnometer method. The phase composition of the samples and the structure of the quasicrystals were determined by x-ray diffraction. Two tribological tests were carried out. Firstly the sliding friction coefficient and wear resistance were determined by pin-on-disk tests in air using a CSM Instruments SA Tribometer. A ball of roller bearing (3 mm radius, steel 100Cr6) was secured to the end face of a pin. During the test, a load of 1 N pressed the ball against the surface of a rotating sample. The velocity of the ball relative to the disk was 5 cm/s, and the wear track radius was 1.5 mm. The friction coefficients of some of the samples were measured in other pin-on-disk tests where the speed of the sample relative to the large rotating disk was 80 cm/s with track radius of 2.5 cm at 5 N load. In the case the wear of the samples was measured with their precision weighing. Mechanical properties of the samples were studied with the measuring indentation using NanoHardness Tester at loading up to 2 or to 30 mN. The microhardness of the samples was determined with a Vickers indenter at an indentation load of 0.5 N. Fracture toughness was evaluated from the length of Palmqvist cracks around indents in microhardness measurements.
5. Results and discussion
5.1. Structure and mechanical properties of the material

Obtained with SEM the x-ray maps of the quasicrystal-based DCMs showed that nickel layer covered the particles. The mean nickel percentage in the DCMs measured by EDX was about 3 wt. %. This value can be referred to as the upper estimate of the quantity, which was defined by the measuring technique features. The samples of compacts (3 mm in height and about 4 mm in diameter) were produced by the method described. SEM-image of the glazed quasicrystal-based sample surface is given in figure 2 (left). In figure 2 (right) the distribution of nickel at the same surface patch is shown in light key.

Figure 2. Structure of the compact produced from quasicrystal-nickel DCM: SEM-image of the glazed quasicrystalline-based sample surface (left), distribution of nickel at the same surface patch (in light key, right).

The nickel characteristic radiation tracks almost absent in the glazed surface patches of larger particles, but they are concentrated in all interlayers between them. It may be stated that the metal is distributed uniformly on the particles surface. The density of the samples after pressing under quasi-hydrostatic conditions at pressure of 8 GPa, 4.7 g/cm$^3$, corresponded to the highest density reported for quasicrystals in the literature. The samples were free of cracks and open pores.

The x-ray diffraction pattern of the starting powder (not shown) corresponds to the icosahedral phase of Al$_{65}$Cu$_{22}$Fe$_{13}$. Exposure to high pressures had no effect on the phase composition of the samples, but led to x-ray diffraction peak broadening due to grain fragmentation figure 3 (top). The observed sintering induced decrease in the x-ray diffraction linewidth of the quasicrystals. Figure 3 (bottom) indicates the formation of a “polycrystalline” structure of the material.

Nickel diffusion caused the quasicrystal stoichiometry violation in a part of DCM sample volume even at lower temperatures. Increase of the $t_{\text{sint}}$ from 445 to 645$^\circ$C caused the decrease of quasicrystal content in the samples from 90 % to 45 wt. %, figure 4. At the same time, the formation of the (metastable) $\beta$-phase during heating of samples sintered without the binder at 645–785$^\circ$C, inside the stability region of the quasicrystals, suggests that after deformation the quasicrystals are in an unstable state [13].

The analysis of microhardness indentation morphology on the fine-grained surface patches of the quasicrystal-based ceramics showed that the grain boundaries are not a “weak” element of the microstructure: the grains were hold in the surface without chipping even if the edge of the indenter fell the grain (figure 5 (right)). Given that the less the grain size is, the less amount of
cracks occurred in them during the preparation processes, one should expect essential increase of crack resistance of quasicrystal samples with decrease of the powder grain size.

In figure 6 the load and unloading curves obtained with NanoHardness Tester are given. In the Table 1 the results on hardness and Young modulus measurements can be seen.

In spite of the crystalline phases presence, the hardness of the composites was in level of values proper to the compacts made of the powder without a binder [13]. Young modulus values

Figure 3. X-ray diffractograms of the compacts produced from the quasicrystal-nickel DCM: cold pressing (top), cold pressing with the following sintering in hydrogen at 550°C (bottom).
Figure 4. Dependence of the quasicrystal phase content in the samples on the sintering temperature.

Figure 5. Microhardness indentation morphology of the quasicrystal-based ceramics: The Palmqvist cracks in the corners of microhardness indentation at large particle (left). Absence of Palmqvist cracks in microhardness measurements at fine-grained surface patch (right).

Figure 6. The load and unloading curves obtained in the runs at maximal load of 30 mN.

also corresponded to ones from [13].
Table 1. Hardness and Young’s modulus of the composites.

| #  | Temperature $t_{\text{sint}}$, °C | Hardness, GPa | Young’s modulus, GPa | Max. depth, nm |
|----|-------------------------------|---------------|----------------------|----------------|
|    | time, min                     | 2 mN          | 30 mN                | 2 mN           | 30 mN          |
| 635| 547 / 40                      | 13.5±1.4      | 7.9±1.9              | 165±24         | 138±20         | 77±6           | 449±52         |
| 632| 550 / 40                      | 12.8±1.6      | 8.9±1.9              | 170±5          | 145±22         | 78±4           | 425±40         |
| 636| 645 / 25                      | 13.9±1.2      | 11.7±0.5             | 168±16         | 174±1.5        | 76±4           | 368±3          |

5.2. The “ball-on-disk” tribological test
In the “ball-on-disk” tests the dependencies of the friction coefficient $\mu$ on the path length and profiles of the samples surface were obtained. Figs 7 (top) and 8 (top) give experimental plots of the friction coefficient versus path length for composite samples that were sintered at different conditions. Figs 7 (bottom) and 8 (bottom) give the 3D surface profiles taken in the sample regions including the track and the 2D ones of the track regions cross-section.

Figure 7. The “ball-on-disk” tests data of the composite sintered at $t_{\text{sint}} = 547$°C (# 635): the dependence of friction coefficient on laps, 3D and 2D images of wear track.
Figure 8. The “ball-on-disk” tests data of the composite sintered at $t_{sint} = 645\,^\circ\text{C}$ (# 636): the dependence of friction coefficient on laps, 3D and 2D images of wear track.

In Table 2 the results of tribological tests at ball relative to the disk velocity of 5 cm/s are given.

| Composition | $t_{sint}$, $^\circ\text{C}$ / sintering time, min | Initial $\mu$ | Final $\mu$ | Mean $\mu$ | Sample wear, mm$^3$N$^{-1}$m$^{-1}$ | Ball wear, mm$^3$N$^{-1}$m$^{-1}$ |
|-------------|--------------------------------------------------|---------------|-------------|------------|----------------------------------|--------------------------|
| QC          | 785 / 15                                         | 0.13          | 0.14        | 0.15       | $<10^{-8}$                       | $2.85\times10^{-8}$      |
| QC          | 785 / 30                                         | 0.15          | 0.83        | 0.69       | $4.0\times10^{-5}$              | $3.50\times10^{-6}$      |
| QC          | 645 / 60                                         | 0.14          | 0.17        | 0.16       | $<10^{-8}$                       | $4.06\times10^{-8}$      |
| QC/Ni       | 550 / 40                                         | 0.05          | 0.05        | 0.05       | $<10^{-8}$                       | $3.56\times10^{-8}$      |
| QC/Ni       | 547 / 40                                         | 0.1           | 0.15        | 0.15       | $<10^{-8}$                       | $2.44\times10^{-8}$      |
| QC/Ni       | 645 / 25                                         | 0.1           | 0.53        | 0.5        | $<1.2\times10^{-4}$             | $1.29\times10^{-6}$      |

Note heavy wear of the sample sintered during 25 min. at 645$^\circ$C. Its hardness and Young modulus have the maximal values among the composites, presented in the Table 1. Apparently
the cause of this combination of the properties is the short sintering time. This time was deficient both to formation of rigid bonds between the grains and to degradation of the quasicrystalline phase. Hard particles lost by the sample destroyed quickly the surfaces both of the sample and of the ball (figure 8). But some of the samples, both those produced from the DCMs and ones from the quasicrystal powder, kept low values of $\mu$ during all the run. The values of specific wear of these samples are lower than the lower threshold of the measurement.

5.3. The “sample-on-disc” tribological tests
During the tribological tests where sample relative to disk velocity was 80 cm/s, the friction coefficient $\mu$ of some samples kept the value less than 0.1 in the initial part of the run. Then the wear of the sample or/and of the disc grew and so $\mu$ did simultaneously. The traveled distance with $\mu < 0.1$ of the samples differing by the sintering temperature values is given in figure 9.

![Figure 9. The traveled distance with $\mu < 0.1$ in the test where sample relative to the disk velocity was 80 cm/s.](image)

It is seen that the composites sintered at definite temperatures near 550$^\circ$C kept low values of $\mu < 0.1$ at longer traveled distance, than the samples without the nickel admixture did. In figure 10 the wear values of the samples at the end of the test are given.

![Figure 10. The wear of the samples versus the sintering temperature.](image)

The measured specific wear values of the composites are lower than ones of the samples without nickel. Relying on the data one can conclude that introduction of the nickel binder into the samples increased the wear resistance of the compacts.

6. Conclusions
Original procedure of the powder treatment for obtaining the quasicrystal-based composite ceramics is developed. Its feature is that at the first stage a thin uniform nickel coating was deposited by means of magnetron sputtering on dispersed micron sized particles that were confined in the plasma. The feature allows to distribute the necessary modifying admixture at low concentration of 2–3 wt.% evenly in the powders. Both the initial quasicrystalline powder and quasicrystal-based DCMs were pressed at room temperature under quasi-hydrostatic
conditions at pressures of 8 GPa and then were sintered in hydrogen at normal pressure at 445–785°C. The samples have the density close to one of monolithic quasicrystal and high hardness values. Increase of crack resistance of quasicrystal samples with decrease of the powder grain size was observed. The composites sintered in the temperature range close to 550°C showed the friction coefficient on hard steel of 0.1–0.15 and low wear that is lower than those presented by the samples without the admixture.

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