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COMPOSITES THEORY AND PRACTICE

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COPPER-BASED COMPOSITES STRENGTHENED WITH CARBON NANOTUBES

The paper presents the preliminary results of studies on obtaining copper-based composite materials strengthened with carbon nanotubes modified with copper nanoparticles. The nanotubes modification was carried out by chemically attaching copper nanoparticles originating from copper acetate. Electrolytically obtained copper powders were used as the matrix. The materials were consolidated by one-sided pressing followed by sintering. Microscopic examinations both of the powders and of the finished sinters were carried out using an Olympus GX41 optical microscope. Additionally, quantitative analysis of the sinters structure on non-etched microsections was performed. Computer software Image - Pro Plus was used to calculate the nanotubes surface fraction and their average surface area; the studied micro-particles aspect ratio was also determined. It has been shown that the nanotubes in the sinters, depending on the sintering method, differ in size and arrangement in the composite.

Keywords: nanotubes CNT-Cu, composites, Cu

KOMPOZYTY NA BAZIE MIEDZI WZMACNIANE NANORURKAMI WĘGLOWYMI

Przedstawiono wstępne wyniki badań otrzymywania materiałów kompozytowych na osnowie miedzi umacnianych nanorurkami węglowymi modyfikowanymi nanocząstkami miedzi. Modyfikacja nanorurek była prowadzona poprzez chemiczne dołączenie nanocząstek miedzi pochodzących od octanu miedzi. Jako osnowę zastosowano proszki miedzi otrzymane elektrolitycznie. Konsolidacja materiałów następowała poprzez jednostronne prasowanie i następujące po nim spiekanie. Wykonano badania mikroskopowe zarówno proszków, jak i gotowych spieków przy użyciu mikroskopu optycznego firmy Olimpus GX41. Przeprowadzono także ilościową analizę struktury spieków na zgładach nietrawionych. Do tego celu został wykorzystany program komputerowy Image - Pro Plus, za pomocą którego obliczono udział powierzchniowy nanorurek oraz ich średnie pole powierzchni, a także wyznaczono współczynnik kształtu badanych mikrocząstek. Wykazano, że nanorurki w spiekach w zależności od metody spiekania różnią się wielkością oraz rozmieszczeniem w kompozycie.

Słowa kluczowe: nanorurki CNT-Cu, kompozyty, Cu

INTRODUCTION

Forming powders into objects of a specified shape may be carried out in various ways: by pressing, extruding powder pastes, casting a powder slurry or continuous rolling of a powder. The method of pressing is most widely used. A weighed or measured amount of powder is poured into a mould, the powder is compacted by an upper punch under pressure. During pressing, the loose powder is compacted, reducing its volume two or three times [1]. The intensive development of composites strengthened with carbon nanotubes occurring in recent years has resulted in searching for new materials of high conductance and of possibly high strength.

Carbon nanotubes have aroused broad interest in nanometric structure applications in numerous research and industrial areas [2-4]. Carbon nanotubes are allotropes of carbon formed as a result of rolling a monoatomic graphite plane, referred to as graphen, into a uniform cylinder a few nanometres in diameter. In terms of structure, carbon nanotubes may be broken down into [5-8]:

1. Single Walled Carbon Nanotubes (SWCNT)
2. Multi Walled Carbon Nanotubes (MWCNT).

To achieve a uniform distribution, carbon nanotubes must be chemically modified prior to introduction to the matrix.

Modification of the nanofiller surface consists of connecting functional groups (-OH, -COOH, -NH_2, etc.), capable of chemical or physical binding with the matrix, seems necessary, which would allow increasing interactions on the interface. The modification methods are different and also depend on the type of polymer which is to form the nanocomposite matrix [9, 10].

There have been many attempts to fabricate composites with CNTs, with metals, ceramics, and polymers as the matrix materials. Copper-CNT composites are promising materials for thermal management, due to their potential for high thermal and electrical conductivity [11]. The thermal conductivity of an individual multi-walled carbon nanotube is calculated to be greater than 3000 W/m K, while the textbook value for the thermal conductivity of pure copper is 400 W/m K [12]. It is supposed that a composite reinforced with nanotubes instead of carbon fiber would have a higher strength and better wear resistance [13]. It is desirable to develop a new kind of composite, with the enhanced properties of the carbon nanotube, to improve the performance of the copper matrix material. This material would have advantages in future thermal management technologies due to its high thermal conductivity and thermal expansion properties within the range compatible with various electronic circuitry components [14].

MATERIAL AND TESTING METHODOLOGY

The initial material consisted of an electrolytically obtained copper powder as well as carbon nanotubes powder CNT CO. LTD, with the commercial name $\mathrm{C_{TUBE}}$ 100, obtained using the thermal CVD method. The raw nanotubes were 1 to 25 μm long, 10 to 40 nm in diameter, with a density of $0.03\div0.06$ g/cm^3 and specific surface area of $150\div250$ m^2/g.

Before the studies, the carbon nanotubes were subject to cleaning to remove the pollution originating from amorphous carbon, carbon black and catalyst particles. CNTs cleaning was carried out using a liquid phase and consisted in treating the as-received material with oxidising liquids (a mixture of concentrated nitric acid (HNO_3) and concentrated sulphuric acid (H_2SO_4)) at the boiling point. Cleaning consisted in treating the raw nanotubes with strong acids, both in an ultrasonic washer and also during heating for 10 hours at the boiling point. Defects favourable to the formation of chemical groups, including carboxyl groups, are formed in the structure during nanotubes cleaning. The formed carboxylated nanotubes were treated with ammonia to obtain ammonia groups (CNT-$COONH_4$) on the CNTs surface. The CNT-$COONH_4$ groups were then modified with copper particles. The copper particles originated from copper acetate. The proportion of nanotubes to pure metal used during the modification was approx. 2:1. Copper nanoparticles were attached to the nanotubes surface via chemical modification, which is presented in Figure 1.

Figure 2 presents the morphology of copper powder particles and of carbon nanotubes modified with copper nanoparticles.

The copper powder particles have a dendritic shape of a substantially developed surface (Fig. 2a, b). The particles of the modified nanotubes have a shape close to spherical, and both powder types feature a metallic lustre (Fig. 2c, d). Because of the high degree of fineness, compact agglomerates (micro-particles) consisting of a few smaller particles (nanoparticles) are observed in the structure of modified carbon nanotubes.

Two series of specimens have been prepared in the form of a powder mixture of pure copper and of copper with an admixture of carbon nanotubes with attached copper nanoparticles. The mass fraction of the strengthening phase (modified carbon nanotubes) was a 10 wt.% of composite. Powders prepared in such a way were blended.

The blend of copper powder components and of modified nanotubes was then compacted. One-sided pressing was used at a pre-set pressing pressure of 50 kN and at the rate of 200 N/s. The specimens were pressed on a ZwickRoell Z100 testing machine.

After pressing, the pure copper specimens were 10 mm in diameter and 3 mm thick, while the copper with nanotubes specimens were 10 mm in diameter, 4.1 mm thick.

The next stage comprised compacts sintering in a vacuum furnace and in an electric arc. The first series of specimens was sintered in an arc furnace under a reduced argon pressure (p = 0.5 bar, I = 150 A). The second series of specimens of the same composition was sealed in quartz ampoules (Fig. 3) under reduced argon pressure. Then they were sintered at 800°C during 1 h.

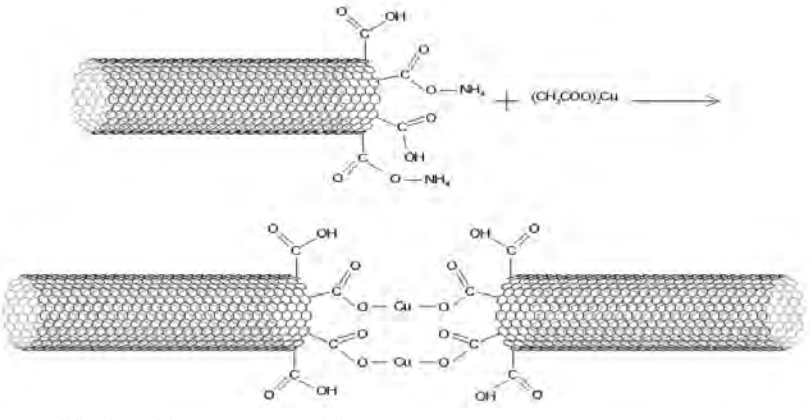

Fig. 1. Ammonated nanotubes modification with copper nanoparticles

Rys. 1. Modyfikacja amonowanych nanorurek nanocząstkami miedzi

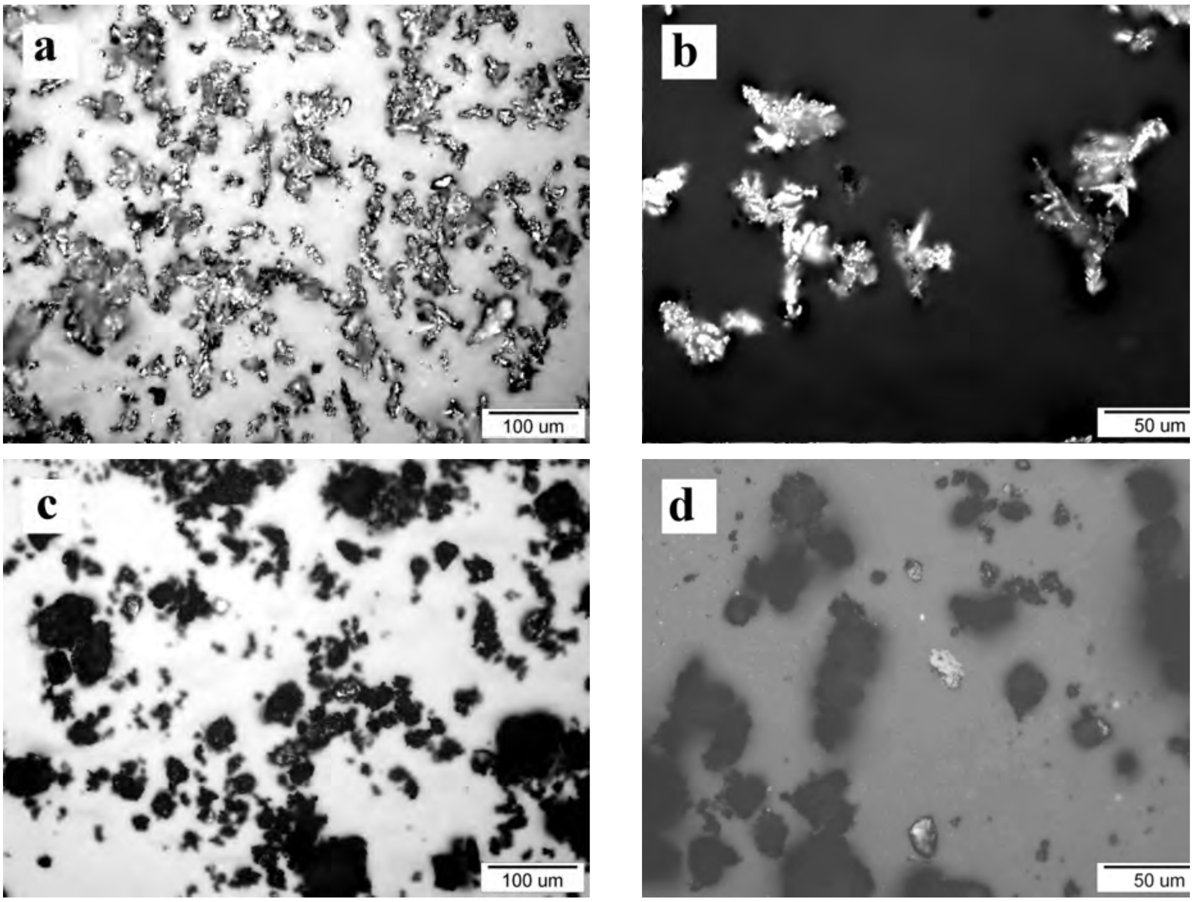

Fig. 2. Morphology of powder particles: a, b) copper; c, d) carbon nanotubes modified with copper nanoparticles

Rys. 2. Morfologia cząstek proszku: a, b) miedzi; c, d) nanorurek węglowych modyfikowanych nanocząstkami miedzi

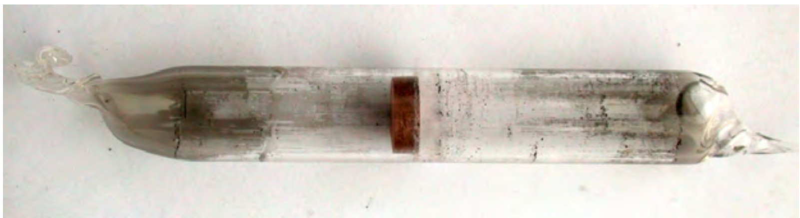

Fig. 3. Specimen sealed in a quartz ampoule after sintering

Rys. 3. Próbka zatopiona w ampule kwarcowej po spiekaniu

RESULTS OF EXAMINATION

The microstructures of the studied composite materials were observed on etched microsections, perpendicular to the direction of pressing. Figure 4 presents the sinters microstructure depending on the applied type of sintering.

The sintered copper features a high grain growth in the case of arc sintering as compared to vacuum sintered copper. However, in both cases, the microstructures of the studied composites show non-uniform distribution of modified nanotubes. In the case of arc sintering, the nanotube agglomerates are arranged mainly on the copper grain boundaries, creating a fusiform structure of micro-particles. In the case of vacuum sintering, the micro-particles distribution is more random.

The next stage comprised a quantitative analysis of sinters structure on non-etched microsections (Fig. 5). Computer software Image - Pro Plus was used to calculate the nanotubes surface fraction and their average surface area; the studied micro-particles aspect ratio was also determined.

Figures 6a and 7a present the distributions of nanotubes aspect ratio broken down into 6 classes and the surface fraction of micro-particles corresponding to a specific class (Figs. 6b and 7b), (numerical values in Table 1). It is possible to notice that in both cases there is a similar trend of micro-particles occurrence - a high number of fine particles of regular shapes ($R < 1.5$), small surface fraction and a small number of large particles of a more developed surface ($R \geq 1.5$), and of much larger areas.

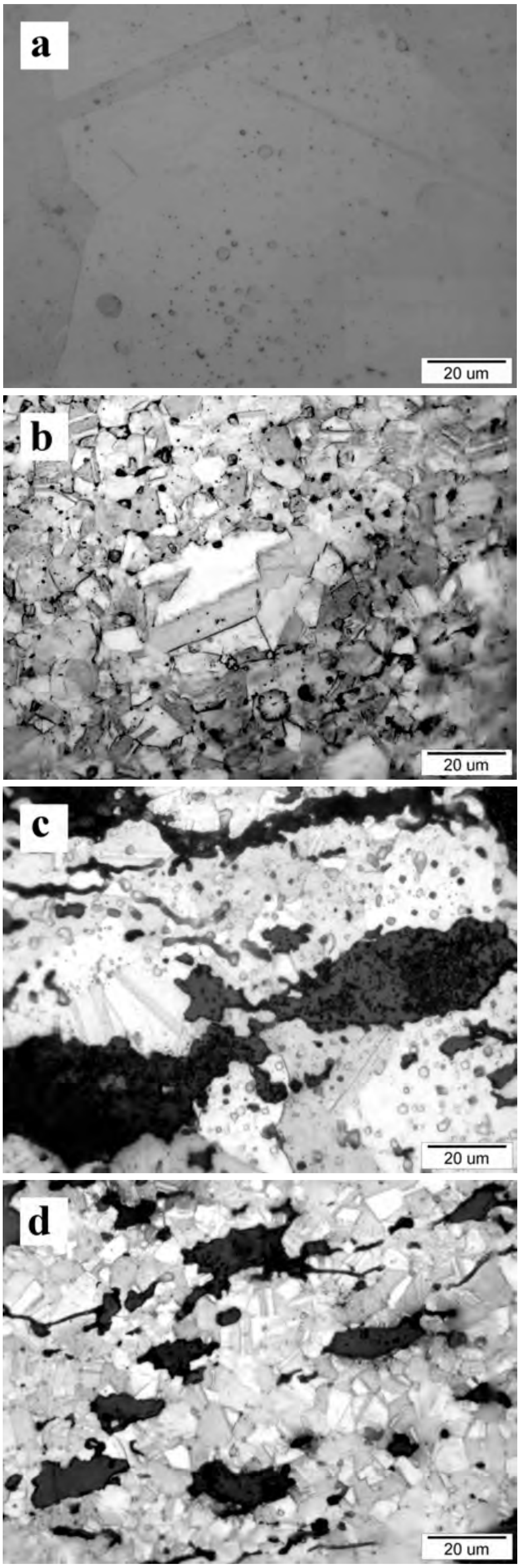

Fig. 4. Sinter microstructures: a) Cu - arc sintering, b) Cu - vacuum sintering, c) Cu/CNTCu - arc sintering, d) Cu/CNTCu - vacuum sintering

Rys. 4. Mikostruktury spieków: a) Cu - spiekanie w łuku, b) Cu - spiekanie w próżni, c) Cu/CNTCu - spiekanie w łuku, d) Cu/CNTCu - spiekanie w próżni

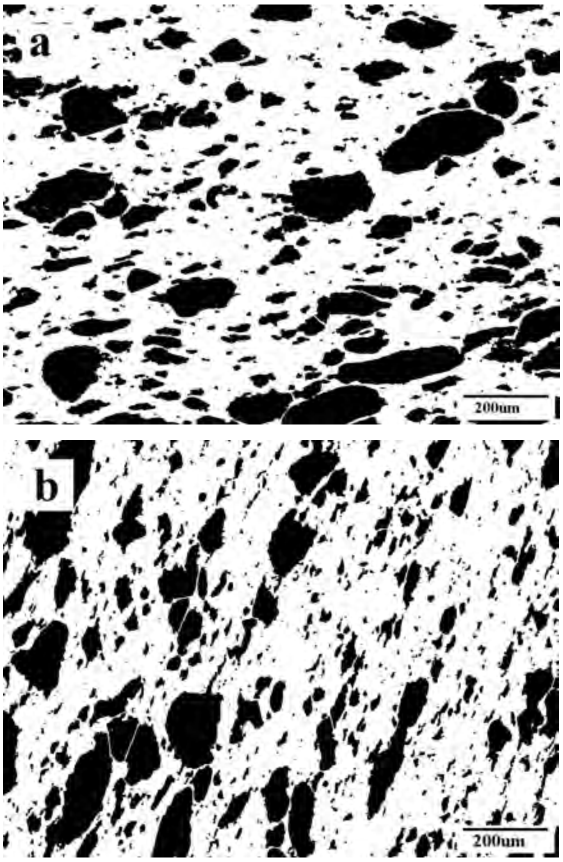

Fig. 5. Micro-particles distribution in studied sinters: a) arc sintering, b) vacuum sintering. Non-etched microsection

Rys. 5. Rozkład mikrocząstek w badanych spiekach: a) spiekanie w łuku, b) spiekanie w próżni. Zgład nietrawiony

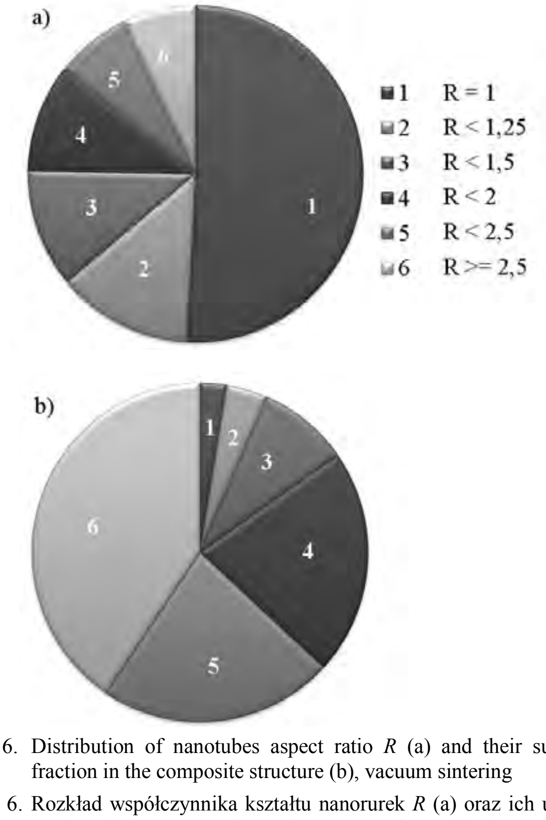

Fig. 6. Distribution of nanotubes aspect ratio *R* (a) and their surface fraction in the composite structure (b), vacuum sintering

Rys. 6. Rozkład współczynnika kształtu nanorurek *R* (a) oraz ich udział powierzchniowy w strukturze kompozytu (b), spiekanie w próżni

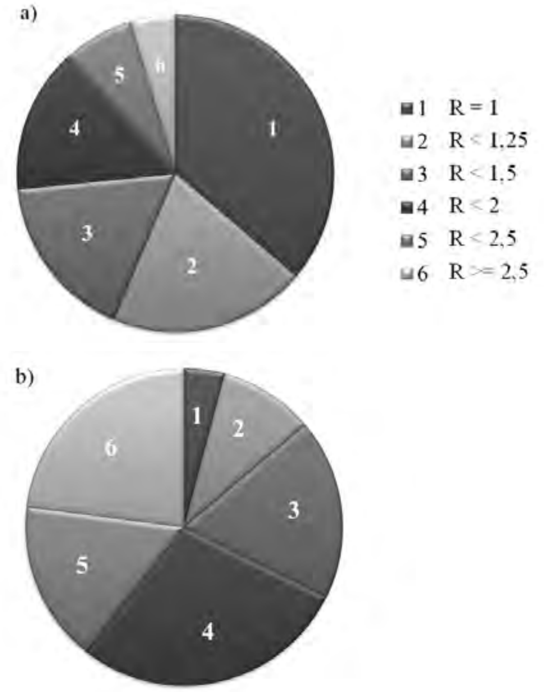

Fig. 7. Distribution of nanotubes aspect ratio R (a) and their surface fraction in the composite structure (b), arc sintering

Rys. 7. Rozkład współczynnika kształtu nanorurek R (a) oraz ich udział powierzchniowy w strukturze kompozytu (b), spiekanie w łuku

TABLE 1. **Results of measurements for nanotubes in composite after arc and vacuum sintering**

TABELA 1. **Wyników badań pomiarów cząstek nanorurek w kompozycie po spiekaniu w łuku oraz w próżni**

No. Class	Aspect ratio *R*	Arc sintering			Vacuum sintering		
		Fraction *R*	Surface fraction [%]	Average surface area [μm^2]	Fraction *R*	Surface fraction [%]	Average surface area [μm^2]
1	$R = 1$	36.2	1.0	289	50.8	0.8	40
2	$R<1.25$	20.2	2.3	1258	13.1	1.2	193
3	$R<1.5$	17	4.4	2684	11.4	2.7	508
4	$R<2$	14.8	6.8	4706	10.4	6.7	1347
5	$R<2.5$	7.2	3.9	5558	7.3	7.0	1977
6	$R\geq2.5$	4.6	5.5	10418	7	12.5	3977

Comparing the sintering processes, it is possible to notice that although numbers of micro-particles of regular shapes are similar (Figs. 6a and 7a), the surface fraction of those vacuum treated micro-particles is much smaller (as against the other particles) than in the case of arc sintering (Fig. 6b and 7b). In addition, the values of nanotube surface area specified in Table 1 show much larger micro-particle dimensions after arc sintering.

CONCLUSION

Cu/CNTCu composites obtained via sintering were studied. One batch of specimens was sintered in a vacuum furnace, the second in an electric arc. In both cases, the nanotubes in the sinters formed compact agglomerates (micro-particles), which differed in their arrangement and size. The obtained results have shown that in the case of vacuum sintering, there is a banded arrangement of nanotube fractions of a much smaller size of the created agglomerates as compared to arc sintering. The arc sintering features a random arrangement of nanoparticles, occurring mainly along the copper grain boundaries. The specimens after arc sintering have a more developed surface, of a maximum average surface area up to 10,000 μm^2. Instead, in the case of arc sintering, the largest micro-particles reach a surface area of ~4000 μm^2.

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