Nanofractals and briquetting technology

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Abstract. The formation of six enclaves in the condensed matter physics and material science has become visible for the last 25 years. These are “nano”, “fractals”, “low dimensional systems”, “chirality”, “hierarchy” of structures and “synergetics”, as well as their combinations. The first five ones characterize the properties of objects and the latter - the experimental conditions. Presently, we can talk about so-called “nanofractals” and their application in technology substantiated by the authors of this work. The problems of briquetting technology are considered from the perspective of one of the aspects of “complexity” - nanofractals. Their adequate application has been carried out for the production of technical silicon using a briquetted charge.

1. Introduction
In the modern development of condensed matter physics and material science, a number of new trends are clearly traced, which relate to both the type of objects of study (materials) and the state and type of impact on these objects. With a great degree of generality, we can assume that the basic and integrating element is the so-called “5+1” system in each of the positions of which there are “nano”-, “fractals,” “systems of small dimension”, “chirality”,“hierarchy” and “synergetics”. Each of these concepts has become the center of specific field development and appropriate materials science [1–4].

It is interesting to note that some combinations could be realized, where these concepts coexist: “nanofractals,” “nanosynergetics,” “synergetics on fractals”, “synergetics on systems with small dimensions”, etc. [1]. Turning to the specific topic of the article, we note that from the mentioned above combined properties of materials and instruments based on the new generation, the success of so-called “nanofractals” has already been achieved to some extent, which is the subject of the present work.

2. Basic concepts
From the most general point of view, it is necessary to distinguish the following three positions of influence and mutual influence of the properties of nano- and fractals on each other:

1. Fractality modifies the characteristics of nano-, i.e., the appearance of fractals on nanoobjects leads to the appearance of nanoscale objects at larger sizes of nanoobjects than just in nanoobjects;
2. The nanoscales of objects lead to an increase in the fluctuations their fractal dimension, all other things being equal;
3. The synergism of nano- and fractality under certain conditions leads to the emergence of objects, i.e., manifestation of fundamentally new properties that their “grandparents” do not have (for example, new types of nonlinearity, and on an earlier issue of prefractals).

By now, Nanofractals have quite clearly acquired the status of modern science with a range of usefulness that extends both to the living and non-living nature. This article is limited to only a few basic models of Nanofractals and their application for technology.

3. Nanofractals on surfaces
Surface science, responsible for physics and chemistry of surface phenomenon, ultimately rests on three basic points: its dimension (topological and fractal), direction of surface electron orbitals and the depth of the surface levels location. We will discuss all these circumstances.

3.1 Tamm’s model
Considering the surface of a crystal as a defect Tamm showed that in the presence of a gap in the electronic spectrum of a crystal, localized states are formed on the surface (with a localization length \( l \)) extending both outward and inward of the crystal. These orbitals are directed normally to the surface and their levels are located inside the electron gap.

3.2 Generalized Madelung-Seitz model
In the case of a significant fraction of the ionicity of the crystal in the surface, some peculiarities appear. It turns out that the energy of occurrence of these levels is associated with the local (on the surface) decrease of the Madelung energy, and because of Coulomb interaction leads to varisomy of near-surface electron structure. The direction of the orbitals can also be considered locally normal to the surface.

In the case of curved surfaces, which was first studied in 2010 (see [1]) (Fig. 1), the spectra of levels become much richer, and the levels of occurrence are now dependent on the curvature of the surface \( K = 2/\rho \) and so is the orbital direction which is normal again, but taking into account the curvature of the surface (all this concerns both topological and fractal dimensions) (Fig. 2).

![Figure 1. Madelung-Seitz diagram illustrates the arrangement of volumetric and surface energy levels of electrons on a halide and metal: a flat surface (dashed lines - 0), a convex surface (solid lines - 1) and a concave surface (dotted lines - 2); \( R_0 \) is the interatomic distance in the crystal.](image_url)
Figure 2. (a) Diagram of directions of neighboring Tamm orbitals ($L_1$ and $L_2$), differing by angle $\theta$, hemispherical nanoparticle in case of its rough (fractal) surface. (b) Passivation of surface $S$ due to the chemical-bond saturation at neighboring Tamm orbitals in the concave regions.

3.3 Fractal Au-Nanocatalysis
In 1985 Haruta (see [1]) discovered that when the size of gold nanoparticles decreases up to $R \leq 7$ nm, gold demonstrates catalytic properties to the reaction $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2$ and other details (for example, catalytic activity $\sim 1/R^3$) (Fig. 2).

Figure 3. (a) Graph for fractality of pore size distribution. (b) Fractal pore in the case $\alpha$ - increased reactivity (catalysis) for such kind of directions of neighboring Tamm orbitals in convex regions and case $\beta$ passivation of surface due to the chemical-bond saturation at neighboring Tamm orbitals in the concave regions.

4. Briquetting as a technological method.
Another important area of using the ideology of complexity, in our opinion, is the area where the so-called briquette technology is used.

An abnormally large inner surface associated with the porosity of the briquette was considered to be the most important circumstance that determines the use of a briquette. It's right, but only in part, since, as it turned out to date, with a decrease in pore size, the surface chemistry itself changes radically: not only does the total pore area increase, but new properties of a nano surface is precisely a consequence of their nanofractality (discovered in Uzbekistan (see [1]), which itself is one of the aspects of "complexity". The main aim of this article is to consider nanofractal properties in briquettes.

The use of briquette technology is associated with at least four channels, which are all due to their porosity. Let's discuss them:

1. Porosity, first of all, leads to a sharp increase in the total area of internal surfaces, which are the place where numerous chemical reactions take place. In this technology, it is fundamentally important that the pores are characterized by a scatter in their radii $f(R)$. For a long time, it was believed that the law of the specified scatter of the radii has a Gaussian character. However, as it turned out by many researchers in recent years [1-4] (Fig. 4), the form of the function can be completely different: it can
be of a fractal type, characterized by a sharp increase in the number of pores of just a small size (Fig. 3). It turned out that such a power law is by no means an accident, but a fundamental property of all objects that carry the property of inequality. A recent book by P. Bak is called “How nature works” (Fig. 3) and it indicates how general this power law is. For our purpose, this is an extremely important conclusion, since it is a large number of small pores that can give its nano fractal result - “emergence”.

Figure 4. (a) The dependence of the fractal dimension $D_f$ on the total porosity of the material $P$ experimentally discovered in [4]. (b) the ratio of energy saving in the technology of smelting silicon alloys with briquetting technology, depending on the total porosity of the material [5].

2. The pore, which is a quasi-closed space (cell), localizes the components - molecules of a chemical reaction, increasing the frequency of their collisions (in several times where the radius of effective interaction of molecules is $R$). This is so-called cell effect (Fig. 3).

When the briquette substances themselves are participants in the chemical reaction in this technology, it is obvious that the convex areas on the inner surface of the pores significantly increase the reactivity in comparison with a flat surface. This conclusion is also realistic because, as it turned out, the perimeter of inner section of the surface of the pores (and not only their total size) is also fractal [1,2], i.e. it is covered with “pimples” of its own material and the number of small pimples is greater than that of large ones. Thus, the law of scatter of pimples in size is also a power law $\phi(p) = \text{const} \cdot p^n$; $n > 1$. It is obvious that such a fractal law also enhances the reactivity according to the laws of nano fractalitity (Fig. 2, 3).

3. When the briquette material itself participates in surface chemistry not only as a component, but also as a catalyst (this is possible when areas of both bulges (pimples) and depressions, i.e. areas with negative curvature, coexist on the inner surface of the pores), it is quite possible to combine the participation of the briquette according to the type of previous point and also according to the catalytic variant. This is the case of nano fractal catalysis proceeding performing the scenario that is required for the maximum implementation of the conceived regime (Fig. 2, 3). Cases of inhibition by nano fractal self passivation of free orbitals on the pore surface can manifest themselves in a very peculiar way.

4. All the discussed features of the chemical reaction in the pores of the briquette concerned an each pore separately. Analyzing the functioning of the briquette “as a whole”, it is already necessary to add the diffusion processes of all components effectively participating in the technology. However, in contrast to “ordinary” diffusion in a medium without porosity, in the case of a briquette with pores, the sizes of which are distributed according to the law of fractals (but not according to Gauss), diffusion through such a medium has a percolation nature and goes through a mechanism called “viscous fingers”. With this mechanism, mass transfer occurs in as in usual as in a special unusual way: there is a slow “middle front” of matter (as in an ordinary medium), but from this front “fast prominences of matter” break out, which reach the ball areas first; the rest of the substance is “pulled up” by ordinary slow diffusion with an average speed $v$. The following circumstance is extremely important: how often are the indicated prominences located on the front of the “middle”? Studies show that the distance between prominences - “viscous fingers” ($\lambda$), the greater (i.e., they are located the less often), the lower
the speed of the “front” in the \(\frac{1}{2}\) degree. Thus, \(\lambda = \text{const} / \sqrt{v} \). The very same velocity \(v\) is determined, firstly, by the differences in thermodynamically driving forces and, secondly, by the peculiarities of the pore size distribution. Thus, diffusion on the “average” is not an adequate mechanism of mass transfer in a fractal medium (with pores). Nevertheless, for an initial rough estimate, such “average” representations are sometimes used.

5. Discussion
What role can the chemical interactions of electron orbitals on the surface of these various pores play here? The answer is a varied role. In particular, they can be temporary traps for diffusing components, inhibiting diffusion (trap mechanism). The second option is overlapping with each other, these orbitals (self-compassing) overlapping with each other (Fig. 2). Obviously, the first option (traps) is typical for large pores (when their inner surfaces are almost flat). The second option (self-seeding mechanism) is characteristic precisely for small pores, i.e. exactly when the concept of nanofractals works, and the pore size distribution is such that it is small pores that are the majority. Thus, with great closeness to the truth, it can be assumed that the pronounced fractality of briquettes providing both self-seeding (in concave areas of the pore surface) and enhanced reactivity (in convex places of small pores) can provide completely new physicochemical ideas about the role and significance of briquetted technology.

6. Conclusions
1. Nanofractals are one of the aspects of the new large concept of condensed matter – Complexity.
2. For the research of many condensed objects, basic models have been built.
3. Particular succes of nanofractals is associated with the study of the physics and chemistry of surface phenomena (in particular, fractals Au-nanocatalysis, self-passivation, electronic structure of surface states on interfaces of living cells, etc.).
4. In this article, the concept of nanofractals is extended to porous media, which is based on briquetting technology (metallurgy of silicon and its alloys).

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