THE CONCEPTIONS OF THE FRACTAL IN THE PHYSICS OF SUPRAMOLECULAR EUTECTICS

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The main statements of the theory of inorganic eutectic systems, evidencing in the proof of the supramolecular conception and taking into consideration the interaction of fractal super-assemblies are considered. The experimentally observable geometric samples-fractales are given; the nature of interphase interaction of fractal aggregate with matrix is shown. The above mentioned is proved by the example of regular eutectic systems of $A^{IV}B^{VI}$ – NiSb type and fractal dendritic structures.

Introduction

The structures, widely used in the technique of eutectic alloys, and also eutectic supramolecular conception taking into consideration the interaction of inadequate substructures and opening the formation mechanisms of supramolecular assemblies in boundary layers ("non-autonomous phases") are considered in the given article. The ability of such self-organizing supramolecular objects to the molecular recognition is their main property. The component recognition proposes the "complementarity", i.e. the mutual interaction of assembly participants both geometric one and on the level of intermolecular bond formation [1-2].

The structural peculiarities of eutectic nature, i.e. the interconnection between phase crystalline structure and phase boundary structure and peculiarities of electron structure of eutectic components are usually considered for its understanding [3-4].

The formation of fractal structures in the result of evolution of any physico-chemical systems is possible. Their formation in the macro- and nanosystems is connected with revealing of dissipative self-organization. Many materials, including dendritic structures, have fractal dimensionality on the different stages of their obtaining [5]. It would be interesting to analyze the morphology of known eutectic alloys from the point of view of their fractal character with the use of fractal aggregate conception once again. There are enough such objects in the capacity of examples.

The consideration of eutectic structures from fractales point of view can introduce the some progress in the description of both regular and irregular aggregates. However, it isn't enough only to describe the forms, it is desirable to understand the formation of internal mechanism of fractal eutectic systems. The series of eutectic aggregates has the character fiber-like structure with fuzzy edges [6]. The analogous structures are obtained in the other systems, for example PbTe – NiSb and PbS – NiSb. They are similar with fractal formations on appearance [3-4]. The investigations on the distribution of inclusion grains in the general matrix (for example, NiSb fibers into PbTe) are necessary. This leads to the consideration of fractal dimensionality. It is necessary to reveal how much the eutectic growth mechanism is able to reproduce the fractal structure, satisfying the demands, required to them. The perceptions of fractale and fractal dimensionality are given in the works [7-8].

The nonfractal and fractal granular microstructures are schematically presented in the work [7]. The broken granule boundaries are fractal ones and are caused by the fractional fractal surface dimensionality $2 \le D \le 3$. Such structure is character for the high-deformed boundaries.

Here, the formations of dendrite-like structures are well known. The fractal dimensionalities of forming dendrites correspond to fractal dimensionalities in two- and three-dimensional systems, obtained at computational modeling [5-7]. The information about microscopic picture of dendrite growth is necessary for the further consideration of eutectic morphology. The eutectic crystallization is always dendrite one, meaning that granules of eutectic phases, consisting in colony, develop in the form of thin-branched dendrites in the connection of specifics of dual growth. The eutectic colonies themselves transform into two-phase dendrites in the growth process [6].

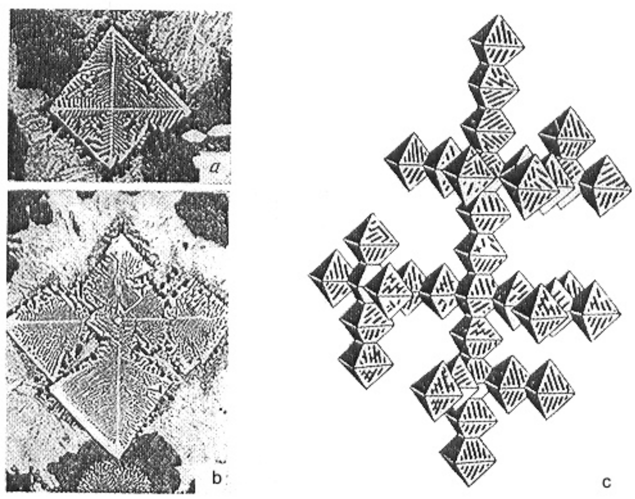

Fig.1. The formation stages of dendrite growth of Fe+(M_0, Fe)C is (a,b), model projection is (c)[6].

For us it is important to know, that each cell grows in the form of eutectic octahedron and first stages of dendrite formation (for example, in eutectic Fe+$(M_0,Fe)_6C$) reproduce the corresponding stages of the formation of leading phase dendrite (fig.1 a,b,c) [6].

The three-dimensional eutectic dendrite, the branches of which are presented themselves the element chains of cube directions of octahedron form, quasi planted one on another along cube direction [6]. The model projection, constructed on the data of stoichiometric analysis is shown in [6] on the fig.1 c.

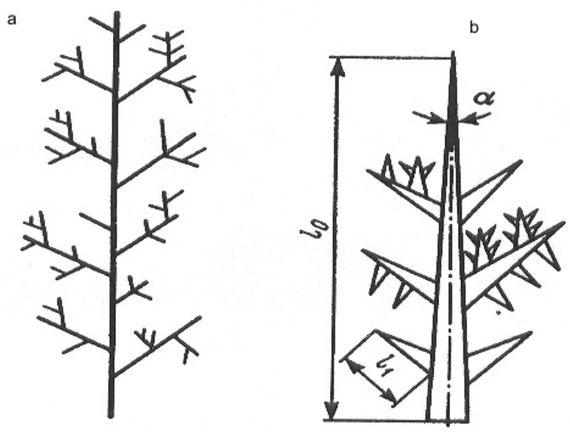

Fig.2. The irregular structure of high-dispersion dendrite particles (a) and junction model of dendrite structure of iron high-dispersion alloys (b) [7]; *L* is the length of particle main stem.

Thus, the dendrite formations in eutectics are integrally similar hereditary fractal structures on the structure as their leading phase. Here it is need to compare the above mentioned results with irregular structures of high-dispersion iron dendrite particles, given in the monograph [7]. The practical use of irregular structures for identification of structures of natural fractals on data [7] is illustrated on the fig.2. The irregular structure, generalizing the model of high-dispersion dendrite particles is shown on the fig.2a. The projection of junction model of dendrite particle on the electron microscope screen, constructed from isosceles triangulars of decreasing sizes (at angle of α) is shown on the fig.2b. The procedure of its construction is given in the [7], here the main stem of particle by length l_0 and square $S_0 = 0,5l_0^2 \sin\alpha$ is divided into some totality of more fine gauges. The series from K_1 trigonal branches of first order by length $l_1=l_0/K_1$ is formed. The considered models of particle space structure of high-dispersion ferromagnetic alloys allow obtaining the qualitative characteristics of their branching degree and fractional fractal dimensionalities [7].

The consideration of eutectic compositions, which are inadequate on all three crystallographic directions in extreme case in the terms of supramolecular chemistry, allows obtaining the answers on many questions and eliminating vaguenesses, mentioned at the discussion of existing eutectic conceptions [2-3].

That's why we here also pay attention on the study of microstructure morphology peculiarities of eutectic alloys with the aim of revealing of nature of interphase interaction of fractale with matrix.

The revealing of phase fractality features in inorganic eutectic suprastructures of $A^{IV}B^{VI}$ - NiSb type is the aim of the given work.

The investigation techniques

The eutectic alloys of the following systems: (PbTe) – Sb, (PbTe) – NiSb are grown by Bridgman method at the velocity *V*=3mm/h at *T*=1200°K and temperature gradient Δ*T*=100° between the heaters.

The microstructures are investigated on the raster electron microscope (REM) JSM-50A with the device for local X-ray analysis and on electron microscope JSM-2000 in the beams of electron secondary emission, in the beams of transmitted electrons, roentgen images in the beams: Te, S, Ni, Sb. The spatial resolution of the mode is ~0,1 mc. The results of these investigations are presented on the fig.2-6.

The fractal dimensionality is calculated by the method, described in the work [8] – (fig.7). *Д* dimensionality is defined by the way of sector (or cell) calculation, which are necessary for the covering of collection in the dependence on sector dimension and it is called sector dimensionality.

The result discussion
The fractal suprastructures in eutectics

The previous investigations show that structures in PbTe – NiSb, SnTe – NiSb, PbS – Ni systems are similar. First of all, let's consider the crystallization in PbTe – NiSb and PbS – NiSb systems.

Fig.3. The longitudinal section of PbTe - NiSb eutectic surface.

PbTe – NiSb eutectic (fig.3) has the fiber structure, PbS – NiSb eutectic has plate structure and composition PbTe 92mol%-NiSb 8mol%. The eutectics of (PbS – Sb), PbTe – Sb systems can be related to anomalous, limited by rod ones with leaf structure of rods and plates. The eutectic PbS – NiSb can be related to normal ones on the form and phase distribution, i.e. to "regular". Each substructure grows with unite strongly delineated solidifying interface, the surface of subblock contact legibly reveals. The definite crystallographic relations, which are character for the given systems exist between phases in the normal microstructures, investigated by us, that isn't observed in anomalous eutectics. The atom interaction of eutectic suprastructures is that indirect physical reason, which supplies the fractal accretion on the definite more energetically profitable directions and supplies the high stability of interphase boundary.

The notion about fractals was firstly used for the measurement of irregular lines, composed from the sections of constant length ε. The length of this kinked curve $L(\varepsilon)$ was accepted for approximate length of monitored object [8]. The dependence of its length on the section dimension in the case of curved line has the form: $L(\varepsilon) = a\varepsilon^{1-D}$ (1), where a>1 is L value for nonfractal curve; D>1 is fractal dimensionality.

The oriented microstructure, characterized by strong regularity of whole "supramolecular assembly" is obtained in the process of directed crystallization. The microstructure of transversal section of oriented eutectic sample of PbTe – NiSb system is presented on the fig.4 (a,b). The composition of eutectic assembly is following: 92mol% PbTe – 8mol% NiSb. The solubility regions are observed in the solid solution on component base.

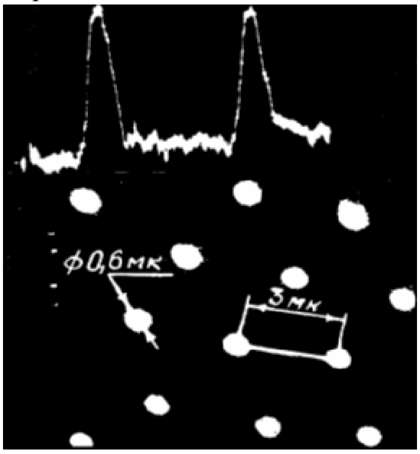

Fig.4. a) the element distribution; b) eutectic transversal section.

The microstructure regularity is reflected on the periodic potential stroke of whole eutectic crystal integrally, and namely: periodic potential of one lattice is rebladed by periodic potential of another one with some period, which is constant for the given eutectic and bigger, than constant lattice of each phase [3].

The morphology analysis of lamellar eutectic of system PbS – NiSb [3-4] and data about electron structure of eutectic alloys allows interpreting the directedly oriented eutectic compositions as class of suprastructural crystalline substances, having the fractal structure. The bond between atoms of different phases [4] appears in the eutectic on the conjugation boundary. Such bond character should be inhered to many eutectic systems according to investigation results. Probably, this leads to the boundary degradation between fractal and matrix.

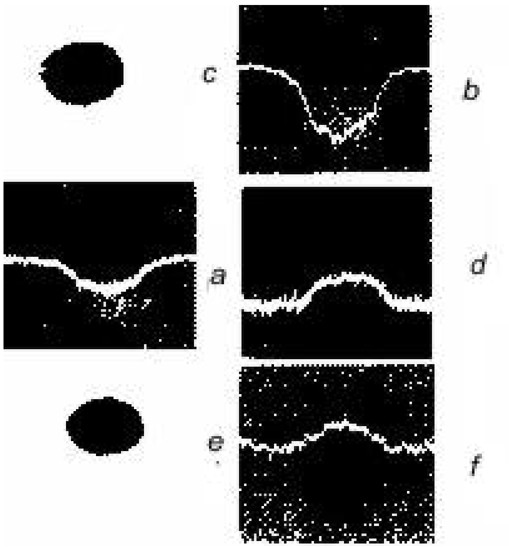

Fig.5. The photos of local X-ray analysis (XLRA) of transversal cut of (LXRA) mode-fractal structure of PbTe - NiSb eutectic in the different modes: a) SE; b) XLRA in characteristic beams Sb with linear image Sb (x14000); c)The same for Ni; d)The same in NiSb beams;e)XLRA in Te beams towards with linear distribution Te; f) SE-mode.

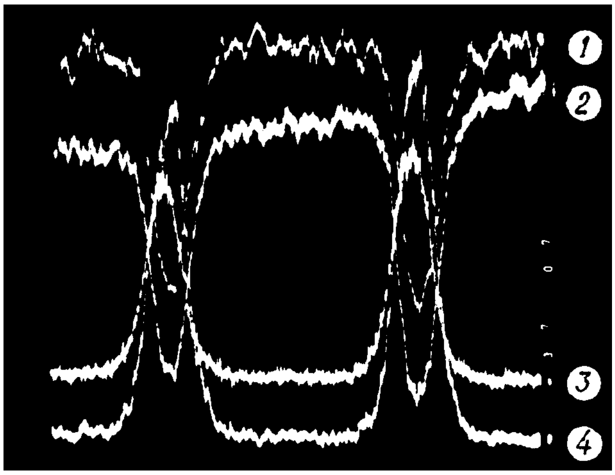

Fig.6. The element distribution in the fractal transversal section (of PbTe - NiSb eutectic).

LXRA photos of transversal section of oriented eutectic PbTe 92 mol% - NiSb 8mol% are presented on the fig.5. The roentgen images in characteristic beams Pb, Te, Ni and Sb towards with their linear distribution obviously evidence about density change particle distribution (fig.5 (a, b, c, d)). The matrix and fractals-inclusions present themselves the limited solid solutions. Each phase is the independent crystal in the system. Moreover, the length of fibers-fractales in PbTe – NiSb vibrates in the limits from 200 nm up to 700 nm at the diameter (160÷180) nm. The fractals have the irregular cigar-shaped form with thickening on the one edge and the needle-shaped sharpening on another one. Each eutectic fractal grows towards with matrix by unite solidifying interface. The boundaries of contact surfaces satisfy the conditions of fractal growth (slow transition of zigzag character). The photos of element distribution in eutectic fractal PbTe - NiSb*,* obtained by local X-ray analysis (LXRA) in the one granule are given on the fig.6. As it is seen from distribution of Pb, Te, Ni, Sb particles in the fractal, the signal fall from Pb and Te and signal increase from Ni and Sb take place in the granule; the distribution densities of Ni and Sb are maximum in the middle and decrease to the edges in NiSb region. The distribution maximum falls on Pb and Te in the matrix and coincides with minimum content of nickel and stibium. The images, obtained in characteristic beams of all four atoms show, that both matrix (PbTe) and inclusions (NiSb) present themselves the limited solid solutions on the base of both components. All data, including (LXRA) are in the total agreement with state diagram of PbTe - NiSb system.

The distortion of matrix and fractal lattices takes place on the interphase boundaries. Here the interaction of force field atoms, which supply the high adhesion and are able to change the complex parameters in the near-boundary series of atoms, takes place.

Thus, the eutectic alloys can be considered as phase (fractale) supramolecular assemblies in the matrix, having the distinctive feature in the comparison with artificially obtained mechanical mixtures, and namely with small distances between fractal dispersion phases and strong interphase bond [3].

It is possible to conclude, that the some chemical interaction takes place in the eutectics on the interphase boundaries that agrees with work results [2-4].

All this says about the fact, that eutectic presents itself the special class of fractal systems, in which the changes of initial component morphology take place in the comparison with them. The appearance of these or that eutectic properties is the result of the character of their chemical bond. This is proved by the morphology of structural fractales.

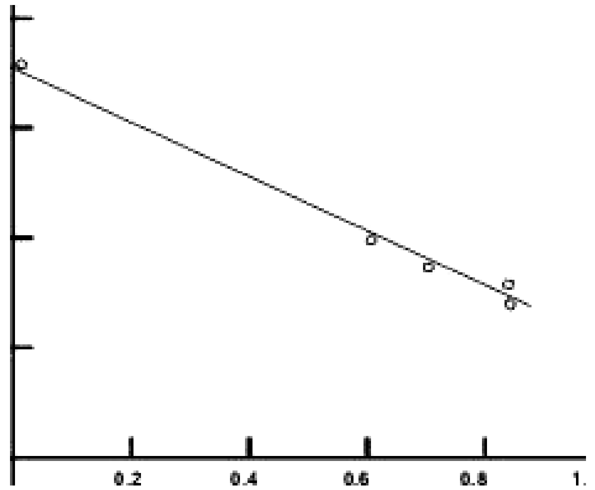

Fig.7. The curve graphical chart in logarithmic scale, corresponding to the $L(\varepsilon)=a\varepsilon^{1-D}$ dependence.

Let's consider the definition questions of fractal dimensionality of investigated phase boundaries in eutectic systems (for example in PbTe - NiSb). In the given case we use the method of region covering by equal square grid with the length of square side *r* (fig.7) for the definition of boundary (fractal) fractal dimensionality. It is calculated, that (as in the work [8]) the square number *N*, the sides of which cross of superblock boundaries even one time; number N=46 for ε=1*mm* (emphasized fourth fractal in the middle) on the given figure 3; the value 1,45±0,01 is obtained for *D*.

This dependence in the logarithmical coordinates is linear (fig.7). The line of slope ratio corresponds to fractal dimensionality. This dimensionality is the dimensionality of only longitudinal cross-section of cigar-like fractal (PbTe - NiSb).

The description of structure geometry with the help of only one value of fractal dimensionality isn't enough. It is followed to find its reason in eutectic nature itself, which is connected with suprastructure interphase interaction. This interaction distorts the lattice on the phase boundary, containing the eutectic: the interatomic bond inside fractale itself, being in the matrix weakens. The lattice elastic deformation is maximal on the boundary and exponentially decreases in the depth of fractal phase. Along with it, the bonds between atoms in the near-boundary region inside phases should cause to the decrease of structure ordering in the given region. The fractal phases PbTe - NiSb, obtained in the eutectic, as it seen from the fig.3 and 6 differ by that property, that their densities decrease on the law, described by the coefficient in the relation particle number – radius [8]. This is the one from the features of fractality revealing of different macro- and nanoparticles. The another characteristic is the fact, that (as it is seen from the fig.3) the fractal here occupy whole matrix object space PbTe, being the part of unite supramolecular assembly in the eutectic, These fractals consist of the parts, which are similar each other in some means.

We here have defined the phase fractal dimensionality by only one object cross-section. However, as we see, the structure of one phase PbTe - NiSb has cigar-like form and it is in elastic-resistant state; phase lattices are elastically distorted, matrix lattices are pressed on the boundary and fibers-fractals are extended. There are no lattice distortions in the transversal direction [3].

The above mentioned experimental results make the use of fractale conceptions in the case of non-self-repeating structures possible. For example the self-affine fractale, the structure of_which is invariant one after simultaneous, but qualitatively different gauge change along different directions in the space. In order to totally character its properties, it is need that how fractal dimensionalities exist, how independent directions are. The self-affine fractales can be obtained by the way of simple expansion of self-repeating fractales, i.e. the relation of expansion values in the different directions should depend on the dimension. In the definite systems the particle aggregates have the brightly emphasized form anisotropy. Such aggregates are called not self-similar, but self-affine ones. In this case it is possible to introduce two fractal dimensions: longitudinal and transversal ones for the description of fractal aggregates [5,8].

The longitudinal fractal dimensionality we have already calculated. It is possible to calculate the transversal dimensionality. The consideration of fractal features of different eutectic systems is the subject of our future investigations.

Conclusion

The analysis and experimental data of physico-chemical processes, taking place in eutectic of PbTe - NiSb system show, that second phase has the fractal structure (with longitudinal fractal dimensionality D_p=1,45). This fractale has the fiber cigar-like form, consisting of the limited solid solution PbTe - NiSb, distributed in the matrix of stibium telluride (moreover, PbTe matrix consists of the limited solid solution PbTe - NiSb). Besides, the boundaries of fractal structures in the whole supramolecular assembly are in elastically-resistant state. The chemical bond, leading to the fractal structure formation appears on the fractale contact boundary. This gives to us the foundation for the consideration of regular eutectic structures as the essential class of supramolecular assemblies, on which the fractal conceptions can be distributed.

[1] *J.M. Len*. Supramolekulyarnaya khimiya. Koncepcii i perspektivi. Nauka, Novosibirsk. 1998,s.115. (in Russian).

[2] *V.S. Pervov, I.D. Mikheykin, E.B. Makhonina, V.D. Buckiy*. J. Uspekhi khimii. 2003, 72 (9), c.852. (in Russian).

[3] *K.Sh. Kagramanov, S.Sh. Kagramanov, E.D. Moroydor, M.G. Pishkin.* Fizika Baki, Elm, 2006, c. XII, №3, p.38.

[4] *K.Sh. Kagramanov, V.V. Didik.* J. Metallofizika. I. "Nauka-Dumka" (Ukraina), 1981, №2, t..3, s. 31. (in Russian).

[5] *V.I. Roldugin.* J. Uspekhi khimii, RAN, 2003, 72 (10), c.931.(in Russian).
[6] *Yu.N. Taran.* Kiyev, Naukova-Dumka, 1970, c. 321. (in Russian).
[7] *V.S. Ivanova, A.S. Balankin, I.J. Bunin, A.A. Oksochonov.* Sinergetika i fraktali v materialovedenii. Moskow, “Nauka”, 1994, c.43. (in Russian).
[8] *Feder Jens*. Fractals., Plenum Press.New York and London, p.258.

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SUPRAMOLEKULYAR EVTEKTİKALAR FİZİKASINDA FRAKTAL KONSEPSİYASI

Neorqanik evtektik sistemlərin supramolekulyar konsepsiyası nəzərdən keçirilib. Eksperimental alınan geometrik fraktal fiqurlar analiz olunub. Göstərilib ki, fraktallar matritsa ilə genetik əlaqədədir. Deyilənlər $A^{IV}B^{VI}$-NiSb evtektikada və fraktal dendrit strukturlarda özünü əks edib.

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КОНЦЕПЦИИ ФРАКТАЛА В ФИЗИКЕ СУПРАМОЛЕКУЛЯРНЫХ ЭВТЕКТИК

Рассмотрены основные положения теории неорганических эвтектических систем, свидетельствующие в пользу супрамолекулярной концепции и учитывающие взаимодействие фрактальных суперансамблей. Приведены экспериментально наблюдаемые геометрические образцы-фрактали, показана природа межфазного взаимодействия фрактального агрегата с матрицей. Вышеизложенное подтверждено на примере регулярных эвтектических систем типа $A^{IV}B^{VI}$-*NiSb* и фрактальных дендритных структур.

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