GEOCHEMISTRY

The Nanoblock Structure of Natural Isoferroplatinum (Pt$_3$Fe) and Problem of Quasicrystalline State of Some Platinum Group Minerals

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Parquet-type nanoblock structure of isoferroplatinum crystals was first discovered with atomic force microscopy (AFM). Fourier and wavelet transforms were applied to the AFM topographic data to reveal the characteristic scales and self-similarity of elements of nanoblock structure, indicating a quasicrystalline structure of isoferroplatinum [1–3].

The studied isoferroplatinum was represented by large (2–3 mm) crystals from the layered dunite–harzburgite–gabbro massif in the Russian Northeast. Phase homogeneity was controlled on a JSM-5620 scanning electron microscope equipped with an EDS LINK 10 000 and on a MS-46 Cameca microprobe. The majority of studied grains were monomineral isoferroplatinum consisting of 75.0 at % Pt and 25.0 at % Fe.

The surface topography of isoferroplatinum crystals was studied on a Femtoscan 001 scanning atomic force microscope using CSC-12 silicon cantilevers (probes). The Femtoscan 001 program provides 2- and 3-D images of the surface and their sections with the determination of both horizontal and vertical nanometer dimensions. The individual sections of the images were analyzed using the Fourier power spectrum. Topographic data were additionally studied with wavelet-analysis [4–6].

The isoferroplatinum grains were specially polished and pressed in an acryloxide matrix. The scanning area for each sample varied from 400 × 500 nm (resolution 1 nm) to 5000 × 5000 nm (resolution 10 nm). More than 200 topographic images were recorded in different scales from the surface of seven isoferroplatinum samples.

All studied samples exhibit a special type of structured surface, namely, nanoblocks or parquets (Fig. 1). It is very visible that the surface is made up of the finest units of few tens nanometers in size, three-fold combination of which yields larger blocks of the higher orders. This type of structure is preserved on all the studied scales. The structure is unaffected by deformations, indicating its high strength [7]. A steady morphology on all the scales indicates self-similarity of the surface of studied isoferroplatinum crystals. Such a structure is defined by the geometry of space tiling [8].
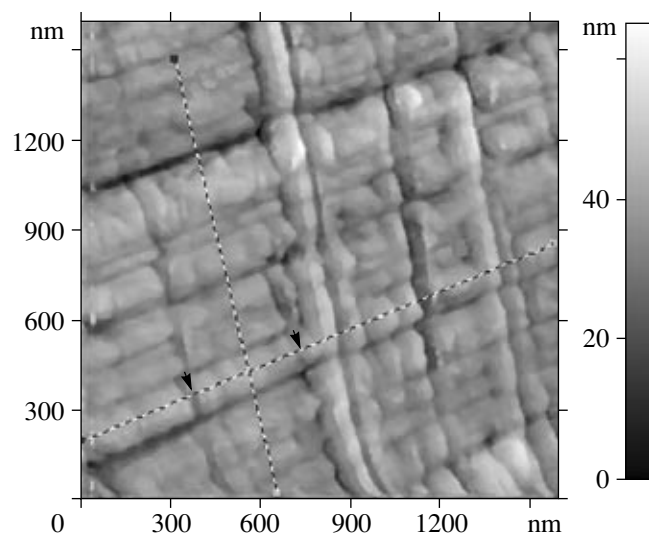

Fig. 1. AFM topographic image of the surface demonstrating nanoblock structure of the isoferroplatinum surface and sizes of nanoblocks.

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(a)

(b)

(c)

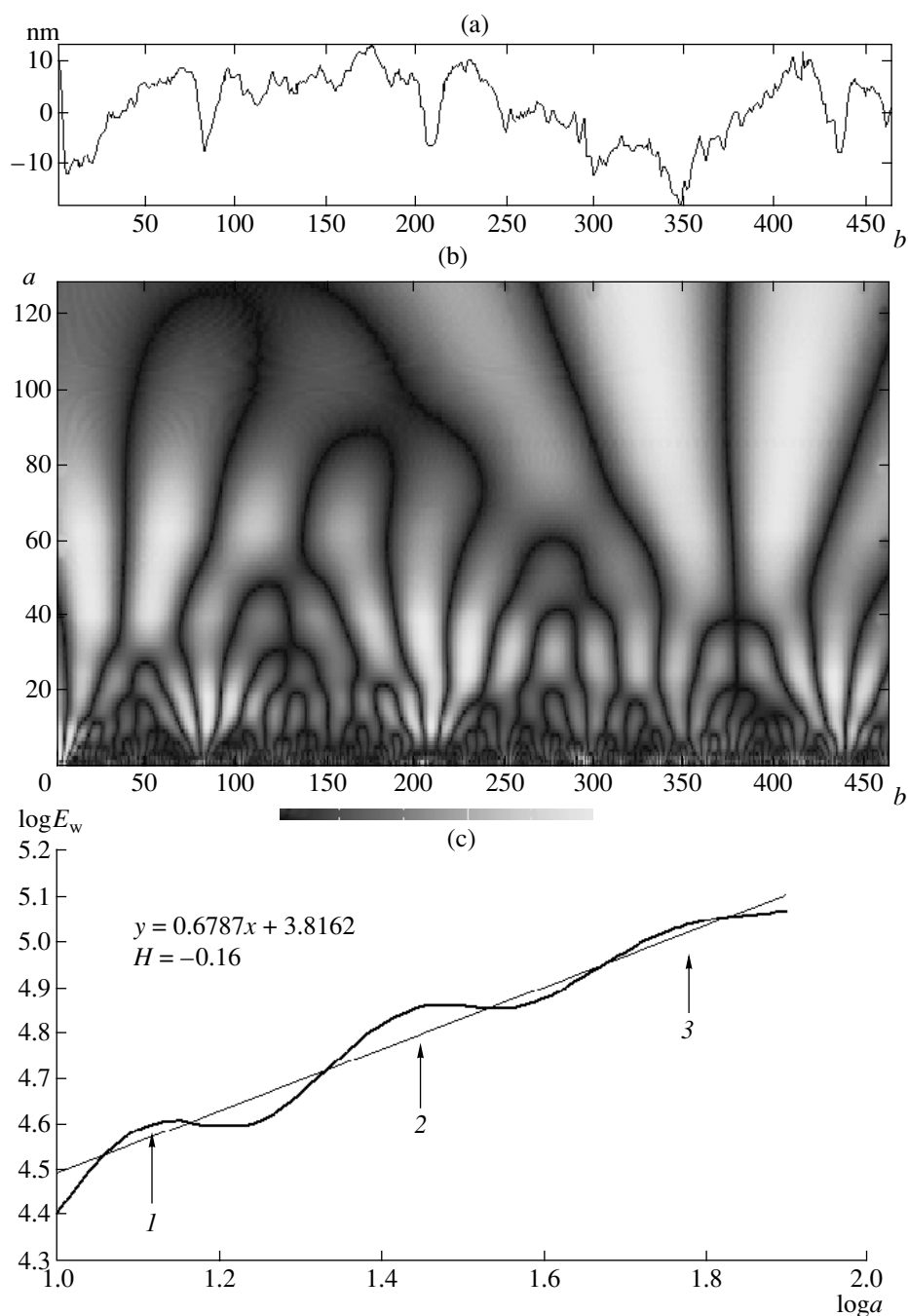$y = 0.6787x + 3.8162$
$H = -0.16$

Fig. 2. Wavelet transform of the AFM topographic data: (*1*) typical section of AFM topographic image of isoferroplatinum; (b) wavelet spectrum; (c) wavelet energy spectrum. Maxima *1–3* denote the presence of characteristic scales of nanostructure; Holder exponent $H = -0.16$ indicates the extent of their interrelation (self-similarity).

Self-similarity was quantified by 1- and 2-D wavelet analysis of AFM topographic data. The wavelet analysis is the spectral analysis of self-similar signals used in AFM spectroscopy for processing digital images. Principles of the theory of wavelet analysis are reported in [3, 4]. Unlike classical statistic methods, wavelet analysis makes it possible to determine the similarity parameters of the analyzed structure (self-similarity)

and to reveal the hierarchy of scales of its manifestation. Thus, the method is efficient for the identification of fractal structures.

The procedure of the quantitative determination of dimensional characteristics (scales) of the individual elements of fine structure included the analysis of individual AFM topographic sections of the surface (Fig. 2a) and the subsequent construction of wavelet power spec-

tra (scalegrams), which record the existence of characteristic scales and the self-similar type of their interrelation (Fig. 2c).

The existence of self-similarity is demonstrated well by fractal relations of dimensional parameters and also by the self-similarity index H [3]. The self-similarity is expressed by linear dependence in the scalegrams in log–log coordinates, where H is the slope angle. The self-similarity parameter H varies from –0.5 to +1, characterizing relative contribution of small and large scales. The H value has a positive correlation with large scales and negative correlation with small scales.

Scalograms of ACM-topogram sections of isoferroplatinum indicate the self-similar character of analyzed surfaces. Histograms of the specified scales show hierarchic distribution of structure-forming elements of the isoferroplatinum surface. Decrease of the H value from 0.25 in small scales to –0.36 in large scales indicates attainment of limit scales of the observed fine structure. The characteristic scales for presented AFM topographic images are 55, 70, 120, 135, 250, and 750 nm. Fourier and wavelet analyses of available characteristic scales show that parquet structure is made up mainly of three types of polygonal nanoblocks with linear sizes of ~30, 50, and 100 nm.

Obtained data suggest that the fine structure of isoferroplatinum crystals represents a regular combination of nanoblocks. The fine structure can be considered as nonperiodic but ordered self-similar structure. The fractal character of self-similarity is clearly recorded in the wavelet spectra (Fig. 2) and almost ideally reproduced for small-scale units. However, it is slightly distorted with increasing size, presumably reflecting changes in growth conditions of real crystals. The parquet nanostructure and self-similarity on the wide range of scales make it possible to consider the studied objects as quasicrystals.

However, the studied isoferroplatinum is not a single example of the nanoblock structure of Pt-bearing phases. In particular, chains of nanoblocks of $Os_{1-x}Ir_x$ composition from few tens to hundreds nanometers in size (Fig. 3) were found by transmission electron microscopy in iridosmine crystals [9]. Size proportions of individual self-similar units of the fine structure suggest that iridosmine crystals belong to quasicrystals. These iridosmine crystals are intergrown with exotic phases, such as Cu_3Os, PbNi, and other phases of variable composition (Os, Ir, Ni, Fe, Cu) with a wide miscibility range of components within a single mineral aggregate, indicating disequilibrium crystallization of these phases.

Obtained data suggest the existence of nonperiodic structures (e.g., quasicrystals) in nature. Their aperiodicity is related to the absence of translation in the solid body. However, such crystals can possess rotational symmetry and fractal ordering. It should be emphasized that a large group of synthesized metallic solid solutions (two- and three-component alloys), which repre-
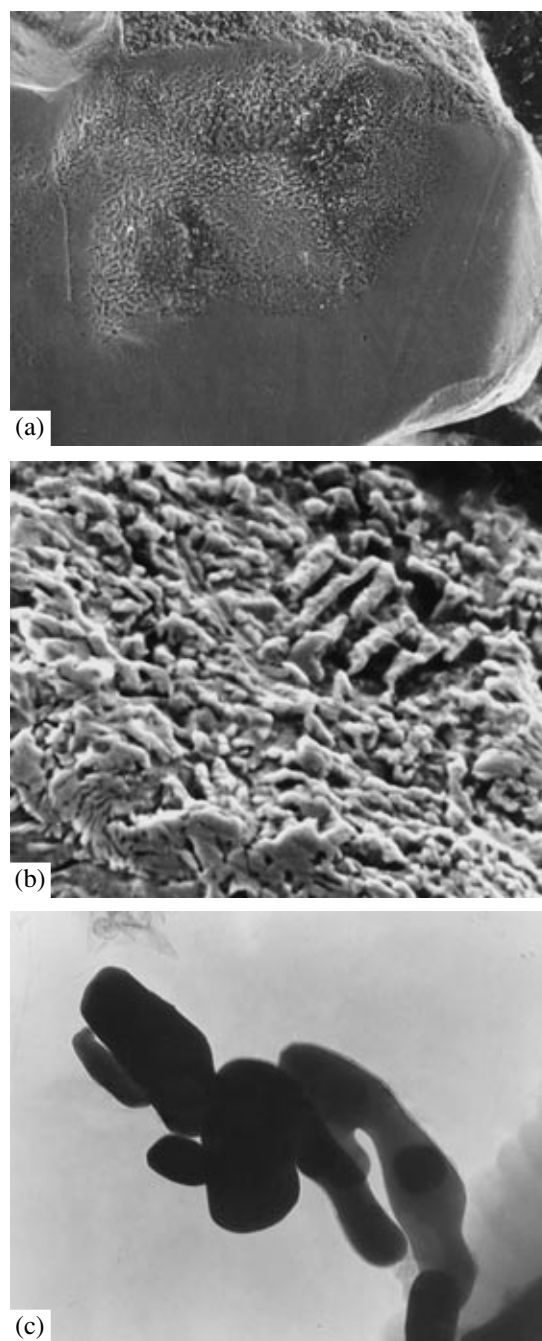

Fig. 3. Fine structure of the iridosmine crystal surface (after [4]). (a) Proportions of dense and block domains on the crystal surface (scanning electron microscopy, magn. 1800); (b) nanoblock structure of the surface (scanning electron microscopy, magn. 15 500); (c) nanoscale elementary units of block structure of the surface (transmission electron microscopy, magn. 14 000).

sent quasicrystals consisting of Pd, Ru, and Os in association with Ni, Cu, and Al, has been experimentally produced [2]. The formation of such phases is presumably related to the high (primarily, temperature) gradient, which governs the ultimate formation of numerous compounds with different structures. Such processes

follow heterogeneous gas–solid and gas–liquid–solid reactions under disequilibrium conditions, e.g., gas transport reactions and processes [11]. They imply that any nonvolatile component is linked with a volatile component under high-temperature conditions, to be transported into the lower-temperature environment and precipitated in the initial state as a result of reactions mentioned above. Disproportionation is a particular case of these reactions. These reactions produce native metals or intermetallic compounds under certain temperature gradients, regardless of a highly reducing regime. Such reactions with the participation of noble metals are observed during condensation of the present-day fumarole systems of active volcanoes [11, 12]. These mechanisms could also play a decisive role in the PGM mineralization of a specific composition (at least, containing the studied isoferroplatinum) and the PGM mineralization of previously studied chromitites. However, this statement may also be valid for a wide range of endogenous noble metal deposits, for which other models seem to be inappropriate.

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