

EXPERIMENTAL MODELING OF THE FORMATION OF NANOPHASE IRON (NP-Fe⁰) USING A LASER. E. M. Sorokin¹, O. I. Yakovlev¹, E. N. Slyuta¹, M. V. Gerasimov², M. A. Zaitsev², V. D. Shcherbakov³, K. M. Ryazantsev¹, S. P. Krashennnikov¹, V. Y. Shklover⁴. ¹Vernadsky Institute RAS, 119991 st. Kosygin 19, Moscow, Russia, (egorgeohim@ya.ru), ²Institute of Space Research RAS, 117997, st. Profsoyuznaya 84/32, Moscow, Russia, ³Moscow State University, Geological Faculty 119991 Lenin Hills Moscow, Russia, ⁴"Systems for Microscopy and Analysis" (SMA), 121353 Skolkovskoe highway 45, Moscow, Russia.

Introduction: One of the signs of “space weathering” on the Moon is the formation of nanophase metallic iron (np-Fe⁰) in the regolith of the Moon, observed in condensate films on the surface of regolith mineral grains and in the agglutinates glass. Np-Fe⁰ is ubiquitous in samples of lunar regolith in the form of globules ~ 5–20 nm in size [1-3]. During micrometeorite bombardment, it is formed as a result of condensation of vapor arising from the shock evaporation of lunar rocks. Especially often, nanophase iron can be observed in a thin amorphous film on the surface of mineral particles [4,5]. Part of the iron nanoglobules is observed in a glass of regolith agglutinates. Nanoglobules are believed to have fallen into glass upon repeated impact melting of regolith and capture of globules initially condensed on the surface of regolithic particles [6]. It is also believed that the chains of iron nanoglobules quite often observed in glass were inherited from zonal-structured condensates on regolith particles. The presence of nanophase metallic iron is subdued characteristic absorption features in reflected spectrum from airless bodies, reduces reflection in the visible region and increases in the red and infrared regions (the so-called redness) [7-10]. In addition, the intensity of these changes depends on the size and concentration of such spherules - the larger the spherules (up to 1 μm in diameter) the stronger the spectrum is change, and same for concentration [10,11]. Moreover, the study of these formations is interesting from the point of view of using regolith in terms of building material for additive manufactures [12].

In this regard, it seems promising to use a laser for modeling the processes of space weathering of airless bodies [9,10,13-17].

Experimental methods, technique and study of the samples: For the experiment, a sample of natural tholeiitic fine-grained basalt without glass (hereinafter referred to as basalt) was selected. The average chemical composition of basalt was obtained by X-ray fluorescence analysis (wt.%): SiO₂ – 48.71, TiO₂ - 1.05, Al₂O₃ - 14.01, MgO – 6.54, MnO – 0.20, FeO – 11.04, CaO – 11.54, Na₂O - 2.03, K₂O – 0.26, P₂O₅ – 0.12, LOI (loss on ignition) – 2.12. The mineral composition (by X-ray diffraction method) is: plagioclase, pyroxene, hematite, ilmenite, quartz and some layered aluminosilicates (approx. modal composition: Pl-55%,

Px-39%, Qrz-2%, Hem-2%). One of the basalt fragments was melted in a quartz crucible at 1300°C for 30 minutes in an atmosphere of pure nitrogen. Thus, there were two types of targets - completely crystallized basalt (hereinafter crystalline basalt) and glass obtained from this basalt (hereinafter basalt glass).

For crystalline basalt and basalt glass irradiation, a pulsed neodymium glass laser was used. The laser radiation wavelength was 1.06 μm, the pulse duration was 10⁻³s, and the pulse energy was ~600–700 J. The energy flux density was ~10⁶–10⁷ W/cm². The temperature at the “impact” point was of the order of 4000–5000 K, which corresponded to the evaporation temperature during high-speed impact processes with collision velocities of the order of 10–15 km/s [13](Fig.1).

Ejection products from craters (glass spherules) and craters were studied by scanning and transmission electron microscopy.

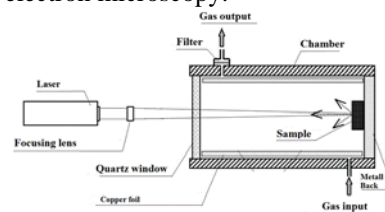


Fig.1. Experimental facility. Ejected products were precipitated on a copper foil substrate.

Results and discussion: When examining the crater from the experiment with basalt glass (it was obtained by melting and rapid quenching of crystalline basalt), placers (trains) of nanophase iron are clearly manifested (Fig. 2). In this case, two fronts of chains of such iron are distinguished. The first front is on the edge of the crater, that is, almost at the air-glass boundary. The second one borders the bright region, which is enriched with aluminum and calcium oxides (respectively, depleted in silicon oxide). Moreover, the second front partially outlines the contours of such an area. Particle sizes approximately vary from tens to hundreds of nanometers. It is assumed that the particle size can be related to the thermal history of the particle so that the formation of large particles (hundreds of nm) can be associated with coalescence effects when large particles are assembled from smaller ones [9].

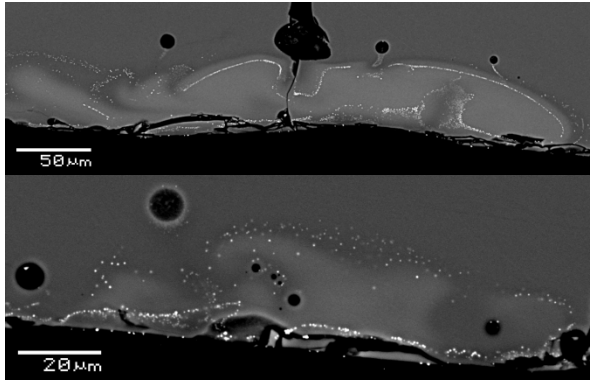


Fig.2. Crater zones in a basalt glass target where nanophase iron placers were detected – SEM.

According to preliminary data from a transmission electron microscope, these are alpha-iron single crystals (Fig.3). They contain minor nickel impurities, sulfur and phosphorus. It should be noted that phosphorus gravitates to the periphery of the particle, as if bordering it.

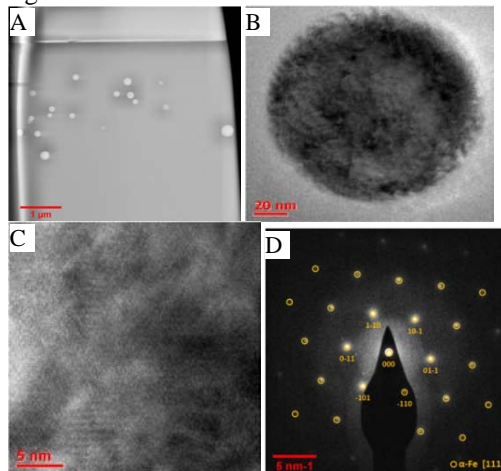


Fig.3. TEM images. A- FIB cut film with agglomeration of np-Fe⁰. B- Close-up view of the np-Fe⁰. C- The part of the particle where the crystal structure is observed (atomic rows). Monocrystallinity is observed here. D- Image of electron diffraction of this particle (shows that it is alpha-iron).

It is likely that this form of arrangement of iron nanospheres can be due to the passage of the shock wave. Such a wave is most likely to occur when a laser pulse interacts with a target material [18]. With a laser “impact”, high pressure arises due to the recoil momentum of the expanding plasma and leads to the formation of a shock wave propagating deep into the target. At the same time, the energy transfer efficiency of the laser pulse to the shock wave is small (about 2-5%). The formation of a crater is associated with phase transformations of compressed and heated matter behind the front of the shock wave. The latter, in turn, determines the parameters of the crater [19].

It should be emphasized that in this case, the formation of spherules occurs exclusively by thermal means in the thickness of the melt. Based on the experimental conditions, there are no reducing agents, and the arrangement (glass-matrix relationship) of the spherules themselves suggests their formation in the melt without an evaporation-condensation mechanism (Fig.2). It is believed that the formation takes place either by the action of a reducing agent [20-22], or by deposition of the shock-formed vapor already containing reduced iron [4,5,7, 23-26].

Conclusion: Thus, a new way for the formation of nanophase iron is shown — in the bulk of the melt without a reducing agent by thermal means. Similar views were expressed earlier in some publications [27]. In addition, we assume that the arrangement of such particles is due to the passage of the shock wave.

References: [1] Runcorn S. K. et al. (1970) *Geochim. Cosm. Acta*, 3, 2369-2387. [2] Housley R. M. et al. (1971) *Geochim. Cosm. Acta*, 3, 2125-2136. [3] Tsay F. et al. (1971) *Geochim. Cosm. Acta*, 35, 865-875. [4] Keller L. P. and McKay D. S. (1993) *Science*, 261, 1305-1307. [5] Keller L. P. and McKay D. S. (1997) *Geochim. Cosm. Acta*, 61, 1-11. [6] Basu A. (2005), *J. Earth Syst. Sci.* 114(3), 375-380. [7] Hapke B. (2001) *J. Geophys. Res.*, 106, 10039-10073. [8] Pieters C.M. et al. (1993) *J. Geophys. Res.*, 98, 20817-20824. [9] Pieters C. M. and Noble S. K. (2016), *J. Geophys. Res. Planets*, 10, 121. [10] Moroz L.V. et al. (2014) *Icarus*, 235, 187-206. [11] Noble S.K. et al. (2007) *Icarus*, 192, 629-641. [12] Taylor, L.A., and Meeks T.T. (2005) *Jour. Aerosp. Engr.*, 18, 188-196. [13] Gerasimov M.V. et al. (1999) *Lab. Astrophys. Space Res.*, 236, 279-330. [14] Kissel J. and Kruger F.R. (1987) *Appl. Phys.*, 42, 69-85. [15] Moroz L.V. et al. (2009) *Icarus*, 202, 336-353. [16] Sasaki S. et al. (2001) *Nature*, 410, 555-557. [17] Yakovlev O.I. et al., (2002) *Bulletin of the Earth Sci. RAS*, 1, 1-3. [18] Clauer A. H. and Holbrook J.H. (1981) *In Shock waves and high-strain-rate phenomena in metals* Ed. M. A. Meyers and L. E. Murr 675-703. [19] Burdonsky I. et al. (2013) *Probl. of Atomic Sci. Tech.*, 36, 8-19. [20] Housley R. M. et al. (1974) *Proc. LPSC 5th*, 2623-2642. [21] Morris R. V. (1980) *Proc. LPSC 11th*, 1697-1712. [22] Taylor L A and Cirlin E-H. (1985); *In: ESR Dating and Dosimetry*, Ikeya M and Miki T (eds), 19-29. [23] Hapke B. (1975) *The Moon*, 13, 339-353. [24] Christofferson R. et al. (1996) *Meteoritics Planet. Sci.*, 31, 835-848. [25] Yakovlev O I, et al. (2002) *LPS. XXXIII*, #1271. [26] Yakovlev O.I., et al. (2009) *Geochem. Int.* 47, 134. [27] Li et al. (2016) *79th Ann. Meet. Met. Soc.* 6338.