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AUGMENTED MODEL OF MICROSTRUCTURE EVOLUTION OF CHORNOBYL LAVAS

The model for the microstructure evolution of Chornobyl "lavas" or lava-like fuel-containing materials (LFCM) have been augmented taking into account new data on black ceramics. Currently, LFCM are multiphase materials; a silicate glass phase contains inclusions of crystalline phases (with and without uranium), nano-sized pore channels, pores and cracks. LFCM has open porosity. The parameters of three of nine previously known physical and chemical processes that occur in brown ceramics: oxidation, radiation-stimulated phase formation and crystallization, were confirmed and refined. Another new chemical process has been identified – the synthesis of uranium-free oxyhydroxide. A new stage of microstructure evolution has been added. Stage durations have been revised. Updated forecast of the state and behavior of LFCM is given. In the future, a group of physical and chemical processes that sequentially occur one after another in brown ceramics and are associated with inclusions of urania will no longer significantly affect the microstructure of black ceramics. There will be little or no destruction of LFCM in the coming years. It has been confirmed that the destruction of LFCM is possible in the medium term; its timing and particle sizes into which LFCM can be destroyed have been confirmed. In the long term, the behavior of LFCM (both brown and black ceramics) will be determined by the crystallization process of the silicate glass phase. Crystallization of several crystalline phases will most likely slow down the crystallization of the glass phase as a whole. Technological and methodological approaches to management of LFCM are discussed.

Keywords: microstructure, evolution model, lava-like fuel-containing materials, physical and chemical processes, crystallization, forecast.

1. Introduction

The news of the accident at the nuclear power plant in the USSR (the city of Chornobyl, Kyiv region, now Ukraine) on April 26, 1986 shocked people throughout the world. Lava-like fuel-containing materials (LFCM), also called "Chornobyl lavas", were discovered in the sub-reactor rooms of the destroyed reactor. They contain most of the radionuclides that were generated in Unit 4 of the Chornobyl Nuclear Power Plant between the last fuel loading and the accident. It took experts ten years of intensive scientific research to create a scenario for the formation of LFCM. A generally accepted view has emerged that LFCM are the result of the interaction of urania fuel pellets (which also contain fission and activation products) with the zirconium alloy of the fuel element cladding and silicates that form part of the reactor structural materials (serpentinite backfill, sand, concrete, *etc.*) [1–8].

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However, it took another thirty years to create a model for the degradation of the microstructure of LFCM. The model was first systematically and comprehensively presented in 2016 in [9]. It is known [1–8] that a relatively large number of physicochemical processes took place in LFCM. The authors of the model selected seven of them. These are processes that significantly influence microstructure formation.

Previously, specialists selected one, two or three processes and attempted to explain the behavior of LFCM on this basis. The proposed model for the evolution of the LFCM microstructure [9] differed in that the authors placed the main emphasis on identifying the relationships and mutual influence between physicochemical processes. It was important to determine the sequence and/or simultaneity of their occurrence. The results of a comprehensive analysis of all available data on LFCM made it possible to form a materials science basis for understanding the evolution of the microstructure.

Work [9] describes all elements of the LFCM microstructure, including the components of the pore space, nanosized pore channels and cracks. The main physicochemical processes that determine the microstructure are identified; the stages of degradation are identified and their durations are estimated; and, for the first time, a forecast of the behavior of LFCM in the coming years and over the long term is provided.

During the period from 2016 to 2020, we obtained new data on the phase composition of brown ceramics [10]. The results of their analysis made it possible to update the model of LFCM microstructure evolution [11]. The main idea about the relationships and mutual influence between physicochemical processes was confirmed. Two more new processes have been added. In addition, new stages of LFCM microstructure evolution have been introduced. The durations of known stages have been clarified and the durations of new stages have been determined. The forecast for the state and behavior of LFCM has been corrected.

In the period from 2021 to 2023, new data on the phase composition of black ceramics were obtained at the Institute for Safety Problems of Nuclear Power Plants of the National Academy of Sciences of Ukraine (ISP NPP, the NAS of Ukraine) [12]. These results stimulated further development of the microstructure evolution model for LFCM to improve the reliability of predictions.

The purpose of this work is to supplement the model of LFCM microstructure evolution by taking into account new data on black ceramics in order to predict its state and behavior in the near and distant future.

2. Change in the Understanding of the LFCM Microstructure, Chemical and Physical Processes in the Period from 1994 to 2023

2.1. Phase composition and microstructure

2.1.1. Data up to 2016

LFCM was a heterogeneous solid solution [1, 2, 4, 5, 8, 13]. The silicate glass matrix (glass phase) contained a large number of inclusions of uranium-containing and uranium-free phases. The sizes of inclusions most often ranged from 3 to 10 microns. Among the inclusions of phases containing uranium are inclusions of urania UO_x, zirconium-containing urania (UO_x with Zr), the zirconium–uranium–oxygen phase $(Zr,U)O_x$ and uranium-containing zirconium silicate, chornobylite $(Zr_{1-x}U_x)SiO_4$. Uranium-free inclusions are silicate dendrites and metal globules.

The *glass phase* of LFCM was silicate glass, which contained sodium, potassium, calcium, magnesium, aluminum, zirconium, iron, uranium and other elements [1, 4, 5]. The glass phase had an uneven distribution of elements. LFCM was “undercooked” glass [9]. This was indicated by a comparison of “preparation” parameters, composition and microstructure of silicate glasses and LFCM. The formation of silicates was complete. The LFCM contained unreacted particles of the starting materials. Consequently, the glass formation stage is only 50–70% complete. The glass phase was not freed from bubbles. This means that the clarification stage had not been completed. The distribution of elements in the material was uneven. There is no talk of homogenization at all. The uranium content in the glass phase is less (often 2–5 times) than the average in LFCM [7, 8]. Estimates show that the inclusions contain 60–70% of the uranium, whereas the glass phase contains 30–40%.

Zirconium-containing urania inclusions (UO_x with Zr) have a very diverse morphology [1, 2, 5, 13]. Researchers have reported cubic and cuboctahedral crystals, particles with condensed morphology, and dendrites. The crystalline inclusions were products of crystallization of the melt of urania UO_x containing Zr. Particles with a fused morphology are nothing more than fragments of solidified droplets of the original melt of urania UO_x containing Zr. Dendrite-like particles were formed during cooling of the silicate melt as a result of crystallization of part of the uranium, which was initially dissolved in the melt. Small inclusions (1–3 μm) located inside zircon crystals containing uranium were products of the reaction between the silicate melt and the phase $(\mathrm{Zr,U})\mathrm{O}_x$. The content of zirconium in inclusions of urania UO_x ranged from 2.5 to 7 wt.%.

Urania and zirconium-containing urania in LFCM inclusions were presented in the form of UO_x oxide [1, 2, 4, 5, 8, 13]. In almost all publications, the authors used an undefined stoichiometric coefficient for oxygen. Only [1, 5] indicated that the crystal structure of a significant fraction of these inclusions corresponded to the oxide $UO_{2.25}$ (according to X-ray phase analysis).

Inclusions of the $(\mathrm{Zr,U})\mathrm{O}_x$ *phase* were amorphous [1, 2, 4, 5]. This was confirmed by X-ray phase analysis. The $(\mathrm{Zr,U})\mathrm{O}_x$ phase was one of the precursors of chornobylite. Inclusions of this phase also contained zirconia in two modifications: monoclinic and tetragonal [5]. The authors of [8] also pointed out the presence of monoclinic and tetragonal zirconia in LFCM.

Inclusions of uranium-containing zirconium silicate, chornobylite $(\mathrm{Zr}_{1-x}\mathrm{U}_x)\mathrm{SiO}_4$ [1, 3, 4, 8]. Chornobylite was obtained during the accident. It is synthesized by the interaction of silicon oxide with the $(\mathrm{Zr,U})\mathrm{O}_x$ phase. Chornobylite contained 0.05–0.1 at.% uranium, i.e. $\mathrm{Zr}_{0.96-0.9}\mathrm{U}_{0.05-0.10}\mathrm{SiO}_4$ [4]. Chornobylite inclusions sometimes contained inclusions of monoclinic zirconia ZrO_2 several microns in size and also containing uranium up to 6–7 wt.% [1].

Silicate dendrites (pyroxene with an approximate composition of
$(\mathrm{Ca}_{0.08}\mathrm{Fe}_{0.02}\mathrm{Cr}_{0.02}\mathrm{Zr}_{0.02})\mathrm{Al}_{0.18}\mathrm{Mg}_{1.86}\mathrm{Si}_{1.82}\mathrm{O}_{5.67}$)
were present in the glass phase [5]. The presence of $\mathrm{CaMg(Si_2O_6)}$ diopside was also noted.

Metal globules [2] consisted mainly of iron with impurities of Cr, Ni, Zr, U, *etc.*

Pore space. Since the 1990s it has been known [2, 5] that brown and black LFCM ceramics contain rounded pores. Researchers also noted the presence of cracks in the glass phase [5], often near inclusions. Systematic studies of porosity [14, 15] were carried out at the ISP NPP, the NAS of Ukraine (Chornobyl) in 2013–2015. To determine the volumes of each set of open pore channels present in the porous body, a method based on evaporation of the working fluid from the pores was used. Samples of brown and black ceramics had open porosity of 13 and 20%, respectively (samples of polychrome ceramics had no open porosity). Brown ceramics contained pores close to spherical in shape, with diameters in three size ranges: 100–200 μm, 40–50 μm and 10 μm. Also, brown ceramics had cracks 2–3 μm in width and nanochannels with diameters of 40–60 nm. The pore space in brown ceramics contained rounded pores (12% vol.), cracks (0.3% vol.) and nanosized pore channels (0.7% vol.). The pore space of black ceramics consisted of gas pores (15.3% vol.), cracks (2.04% vol.), nanosized pore channels (1.32% vol.) and nanopores (1.35% vol.). The diameter of nanopores in black ceramics is estimated at 15–35 nm.

Round-shaped pores (gas pores) were formed during the cooling of the silicate melt at the final stage of the accident of the 4^{th} unit of the Chornobyl nuclear power plant [14, 15]. This occurred due to a decrease in the solubility of gases in the silicate melt as its temperature decreased. Most of the cracks were formed due to an increase in the volume of urania during oxidation in crystalline inclusions. A significantly smaller fraction of the cracks is of thermal origin and resulted from the rapid cooling of the LFCM surface layers. The content of the cracks is estimated to be 10^5 cracks/cm^3. The average distance between them is 100–200 μm. Nanosized pore channels were undoubtedly formed by the merging of some of the tracks of α-particles formed in LFCM during the α-decay of radionuclides. The nanochannels connected the gas pores with the external environment and ensured the formation of open porosity in the LFCM. The nanopores in black ceramics apparently formed during LFCM cooling after the accident, due to the differences in the linear thermal expansion coefficients between the bulk of the glass phase and its peripheral regions, possibly formed due to the silicate melt segregation.

Secondary uranium minerals on the surface of LFCM. The authors of [16] identified a secondary uranium mineral, uranyl sodium carbonate $\mathrm{Na_4UO_2(CO_3)_3}$, in which sodium is partially replaced by potassium. There are also data [7] on secondary uranium minerals: studite $\mathrm{UO_4 \cdot 4H_2O}$, epiantinite $\mathrm{UO_3 \cdot 2H_2O}$, rutherfordine $\mathrm{UO_2CO_3}$ and uranyl sodium carbonate $Na_4UO_2(CO_3)_3$. These secondary minerals were synthesized by the interaction of LFCM with carbon dioxide from the air and water. Information is available [17] on the formation of the uranium secondary mineral (Na–S–U–O) containing not only uranium and sodium, but also sulfur.

2.1.2. Data obtained in Chornobyl in 2018–2019

In 2018–2019, specialists from the ISP NPP, the NAS of Ukraine studied the phase composition of brown LFCM ceramics using X-ray phase analysis [10]. For the first time, uranium-containing phases were identified: urania $UO_{2.34}$ and uranyl silicate potassium hydrate (Wicksite) $K_2(UO_2)_2(Si_2O_5) \cdot 4H_2O$. The presence of previously known phases was also confirmed: cubic and tetragonal zirconia and zirconium silicate $ZrSiO_4$. Aluminum silicate Al_2SiO_5 and possibly calcium silicate Ca_2SiO_4, as well as several phases of silicon oxides, were found for the first time. The content of these crystalline phases was (mass % in descending order): 4.5–5.5 urania $UO_{2.34}$; 3–5 orthorhombic (1) silicon oxide SiO_2; 3–4 uranyl silicate potassium hydrate (Wicksite) $K_2(UO_2)_2(Si_2O_5) \cdot 4H_2O$; 1–2 cubic and 1–1.5 tetragonal zirconia ZrO_2; 0.25–0.35 zirconium silicate $ZrSiO_4$; 0.4–0.6 aluminum silicate Al_2SiO_5 and possibly calcium silicate Ca_2SiO_4; as well as silicon oxides: 0.45–0.75 orthorhombic (2), 0.3–0.5 trigonal and, possibly, 0.8–1.2 tetragonal.

Urania [10] was present in the $UO_{2.34}$ form. Most likely, most of the urania contains zirconium, while a smaller part may not contain it. Oxidation of urania occurred during the accident and continued for many years afterward. Inclusions of urania in LFCM are in a compressed state. In 1997, the authors of [1] reported that urania was present in the form of $UO_{2.25}$ oxide. We believe that the stoichiometric coefficient for oxygen in urania rose from 2 to 2.25 during the accident and increased to 2.34 over the many years following the accident.

Potassium uranyl silicate hydrate (weeksite) $K_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$ [10]. In the 1990s [1, 4, 13] it was not discovered in LFCM. It was formed after the accident due to the interaction of urania from inclusions with water and sodium, potassium and silicon of the silicate glass phase. The synthesis took place at ambient temperatures over a long period (thirty-three years, from the end of the accident until 2019). The synthesis of this compound is stimulated by long-term self-irradiation of LFCM.

Zirconium silicate $ZrSiO_4$ (zircon) [10] most likely contains uranium in its crystal lattice. This is zirconium silicate with uranium, or chornobylite $(Zr_{1-x}U_x)SiO_4$ [1, 3, 4, 8].

Zirconia (cubic and tetragonal) [10] was the result of crystallization of the amorphous zirconium-uranium-oxygen phase $(Zr,U)O_x$ over several decades after the accident. The crystallization may not have been complete. It is known [4, 5] that in the 90s this phase contained grains of monoclinic and tetragonal zirconia. These grains could contribute to the crystallization process as crystalline seeds. The identification of two zirconia phases can also be explained by the uneven distribution of uranium and zirconium in the LFCM.

Silicon oxides [10]: orthorhombic (1), orthorhombic (2), trigonal and, possibly, tetragonal could be formed during the crystallization of a multicomponent silicate melt immediately after the accident (cooling stage), and during the crystallization of the silicate glass phase for more than thirty years after the accident. The high content of silicon oxide in the glass phase promoted the crystallization of its phases. Probably, self-irradiation initiated the process of crystallization of the LFCM glass phase.

Silicates. Aluminum silicate Al_2SiO_5 and, possibly, calcium silicate Ca_2SiO_4 [10] could also have formed during the accident due to the crystallization of a multicomponent silicate melt (during its cooling), as well as due to the crystallization of the glass phase over the thirty-three years following its formation (from the end of the accident until 2019). This became possible due to the presence of silicon, calcium, and aluminum in the glass-phase composition.

2.1.3. Data obtained outside Chornobyl in 2020–2023

The work [18] presents data on the elemental composition of the glass matrix in LFCM and on the crystalline phases present in them: urania with zirconium, UO_x with Zr; cubic urania UO_x, with a structure and chemical composition close to stoichiometric UO_2; high-uranium artificial zircon $Zr_{1-x}U_xSiO_4$ $(0.05 \le x \le 0.1)$; tetragonal zirconia $Zr_{1-y}U_yO_2$ $(0.11 \le y \le 0.14)$; and monoclinic zirconia (artificial baddeleyite) $Zr_{1-x}U_xO_2$ $(0.033 \le x \le 0.05)$. Some crystalline phases of the “yellow spots” on the surface of the black “lava” are minerals: epiianthinite $UO_3 \cdot 2H_2O$, studtite $UO_4 \cdot 4H_2O$, and rutherfordine UO_2CO_3. $Na_4(UO_2)(CO_3)_3$ and sodium carbonate $Na_2CO_3 \cdot 2H_2O$ were also identified.

This publication [18] summarizes data on the phase composition of LFCM for the period from 1994 to 2017 (see [1–8]). All these phases are already presented in Section 2.1.1.

A group of researchers [19] published new results on the chemical composition and structural properties of the Chornobyl “lava” matrix. Data on the crystalline phase of zirconium-containing urania, UO_x+ Zr, are also presented. The elemental composition of the glass matrix (glass phase) of LFCM is close to that given in earlier works [1, 4, 5]. Urania with zirconium, UO_x+ Zr, was identified in LFCM by many authors in the 1990s (see Section 2.1.1) [1, 2, 5, 13].

Researchers from the UK produced simulated LFCM using heat treatment and studied their phase composition and microstructure [20–22]. The initial mixture was prepared from the corresponding oxides, hydroxides, carbonates, and 316 steel (Fe/Cr18/Ni10/Mo3 Goodfellow). The resulting material consisted of a set of crystalline phases embedded in a glass phase. The glass phase had a calcium-aluminosilicate composition. The authors identified crystalline phases of urania UO_2 and zirconium-containing urania (UO_x + Zr), cubic zirconium oxide with uranium $(Zr_{1-x}U_x)O_2$, monoclinic zirconium oxide ZrO_2, chornobylite $(Zr_{1-x}U_x)SiO_4$, and albite ($NaAlSi_3O_8$). The presence of spherical iron globules with impurities of Ni, Mo, and Cr was also noted.

2.1.4. Data obtained in Chornobyl in 2020–2023

Over the period from 2020 to 2023, studies of LFCM black ceramics were carried out using electron microscopy and X-ray phase analysis at the ISP NPP, the NAS of Ukraine in the city of Chornobyl [12]. Crystalline uranium-containing phases were discovered: Rameauite $K_2Ca[(UO_2)_3O_3(OH)_2]_2 \cdot 6H_2O$, urania $UO_{2.34}(U_4O_9)$, and chornobylite $(Zr_{1-x}U_x)SiO_4$. Black ceramics also contain non-uranium phases: magnesium oxide MgO, Katoite $Ca_{2.916}Al_2(SiO_4)_{1.104}(O_4H_4)_{1.89}$, calcium and magnesium silicate $CaMgSiO_4$, magnesium aluminate (spinel) $MgAl_2O_4$, magnesium silicates $MgSiO_3$ and $MgSiO_4$. According to estimates, the content of Rameauite $K_2Ca[(UO_2)_3O_3(OH)_2]_2 \cdot 6H_2O$ can be 5–10 wt.%, magnesium oxide MgO several wt.%, and each of the other phases less than 1 wt.%.

Rameauite $K_2Ca[(UO_2)_3O_3(OH)_2]_2 \cdot 6H_2O$. We were the first to establish that black ceramics contain hydrated complex uranyl oxide $K_2Ca[(UO_2)_3O_3(OH)_2]_2 \cdot 6H_2O$ [12], which is the mineral Rameauite. Such minerals [23] are among the first alteration products formed during the weathering of uraninite (pitchblende) in oxidized zones of uranium deposits throughout the world. In the 1990s [5, 7, 8], the mineral Rameauite was not discovered in LFCM. We have shown that it is synthesized by the interaction of urania (from inclusions) with potassium and calcium oxides of the silicate-glass LFCM phase and water. The synthesis of Rameauite took place over a long period of time (more than thirty years, from the end of the accident until 2022) at ambient temperatures. Apparently, the process of its synthesis is associated with a significant number of defects caused by self-irradiation.

Urania in inclusions. It has been established for a long time [1, 2, 4, 5] that LFCM contain inclusions of urania. Most of them also contain zirconium. Thirty-seven years after the accident, urania in the inclusions is present in the form of oxide $UO_{2.338}(U_4O_9)$ [12]. The stoichiometric coefficient for oxygen is 2.338. The authors of [1] (1997) reported that at that time urania in the inclusions was present in the form of oxide $UO_{2.25}$. Considering that before the accident urania in the reactor fuel rods was present in the form of UO_2, it becomes clear that oxidation of urania in inclusions occurred both during and after the accident. As a rough estimate, we assume that the stoichiometric coefficient of oxygen in urania rose from 2 to 2.25 during the accident and increased to 3 (for most of the urania) and 2.338 (for a smaller fraction of it) over many years after the accident. This larger portion of urania took part in the synthesis of Rameauite. It has been established [12] that 80–90% of U in LFCM inclusions is present in the form of Rameauite $K_2Ca[(UO_2)_3O_3(OH)_2]_2 \cdot 6H_2O$, and 10–20% is present in the form of cubic urania $UO_{2.338}(U_4O_9)$.

Magnesium oxide MgO was discovered in LFCM for the first time [12]. It is possible that this is a product of thermal decomposition of dolomite $CaMg(CO_3)_2$ during the accident. Among the various materials that were dumped into the reactor shaft, there was, in particular, dolomite [6]. In the temperature range 800–900 °C, calcium and magnesium carbonate $CaMg(CO_3)_2$ (dolomite) decomposes into calcium oxide CaO, magnesium oxide MgO, and carbon dioxide CO_2 [24]. Dolomite may not have entered the reactor's inner shaft and therefore may not have participated in the formation of black ceramics. Under this scenario, we cannot explain the origin of magnesium oxide in black ceramics.

Chornobylite $(Zr_{1-x}U_x)SiO_4$ (zirconium silicate, zircon with uranium) was found exclusively in lavas of the 4th unit of the Chornobyl Nuclear Power Plant [3–5, 13]. Chornobylite $(Zr_{1-x}U_x)SiO_4$ in LFCM was formed during the accident due to the interaction of silicon oxide with the $(Zr,U)O_x$ phase. The uranium content in Chornobylite is in the range $x \in [0.05; 0.1]$, i.e. $Zr_{0.96-0.9}U_{0.05-0.10}SiO_4$ [3].

Katoite $Ca_{2.916}Al_2(SiO_4)_{1.104}(O_4H_4)_{1.89}$. It was first discovered in LFCM black ceramics [12]. This is a product of the interaction between water and the glass phase, possibly in LFCM cracks. The glass phase contains all the elements present in this compound except hydrogen. Undoubtedly, Katoite $Ca_{2.916}Al_2(SiO_4)_{1.104}(O_4H_4)_{1.89}$ was formed in LFCM in the destroyed reactor over many years after the accident.

Calcium and magnesium silicate $CaMgSiO_4$*, magnesium aluminate (spinel)* $MgAl_2O_4$*, and magnesium silicates* $MgSiO_3$ and Mg_2SiO_4 [12] – these compounds were apparently formed in the glass phase, which contains all the necessary elements. All these compounds are apparently products of glass-phase crystallization. Apparently, part of each of these compounds was formed as a result of crystallization in the cooling lava during the accident, whereas the remaining part was formed over a long period of time after the accident. Self-irradiation of LFCM contributed to the activation of crystallization processes.

Metallic iron α-Fe (ferrite). It is known [4, 13] that LFCM contain inclusions consisting mainly of iron. Perhaps this phase is α-Fe (ferrite). Iron, as the main element of steels, became part of the LFCM as a result of the melting of the steel structures of the reactor vessel [25].

2.2. Previously known (before 2020) physicochemical processes that predetermine the LFCM microstructure

When creating a model for the evolution of the LFCM microstructure in 2016, from all physicochemical processes that had occurred after the accident over the course of thirty years (at that time), we identified those that had a decisive influence on the formation of the LFCM microstructure [9].

Each of the listed processes was confirmed by the collected and analyzed data that confirmed their occurrence in LFCM [9].

In 2020, the model for the evolution of the LFCM microstructure was updated [11] using the data on the phase composition of brown LFCM ceramics obtained in 2017–2020 [10]. In brown ceramics, from immediately after the accident until the present time, radiation-stimulated synthesis of uranyl silicate sodium-potassium hydrate $(Na, K)_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$ has been taking place. This process complements process group No. 7 [9].

Several phases of silicon oxide SiO_2, aluminum silicate Al_2SiO_5, and, possibly, calcium silicate Ca_2SiO_4 were found in brown ceramics [10]; this indicates a crystallization process in the silicate-glass phase, which has continued for more than thirty years after the accident and is still ongoing. We have also included this process in the list (process No. 8). This process also took place during the accident. In 1990–1993, silicates, pyroxene, and diopside were discovered in LFCM [5]; they were formed in a silicate melt during the accident upon cooling a silicate multicomponent melt.

2.3. Sequence and interrelation of previously known (before 2020) physicochemical processes that predetermine the evolution of the LFCM microstructure

The evolution of the LFCM microstructure, the sequence and interrelation of physicochemical processes, taking into account all the data available at that time on the phase composition and the identified physicochemical processes, were described in detail in 2016 [5] and 2021 [11].

Six months after the accident, the Chornobyl "lava" had become a composite material. The silicate-glass phase contained a number of crystalline inclusions: urania UO_x; zirconium-containing urania, UO_x with Zr; zirconium-uranium-oxygen phase $(Zr,U)O_x$; uranium-containing zirconium silicate (chornobylite $(Zr_{1-x}U_x)SiO_4$); silicates in the form of dendrites; and metal globules.

In subsequent years, tracks produced by α-particles accumulated in the LFCM due to the α-decay of radionuclides. After 10–12 years (1996–1998), at least some of the tracks interconnected and formed a framework of open nanosized pore channels. Perhaps this may have occurred after a certain threshold concentration of α-tracks had been exceeded.

Eventually, air began to penetrate into the urania inclusions through nanoscale pore channels inside the LFCM. The urania UO_x in the inclusions began to oxidize further, their mass and, consequently, volume began to increase. The glass phase restrained the increase in the volume of inclusions. The increase in the volume of the inclusions placed the surrounding glass phases under stress, causing cracks to form. The mechanical properties of LFCM decreased significantly. This occurred between 2004 and 2011. Air could also penetrate into the UO_x inclusions through cracks. The oxidation process became much more active; the urania UO_x oxidized to $UO_{2.34}$.

From this point onward, water began to interact with urania UO_x, owing to its ability to penetrate through cracks into inclusions inside the LFCM. Hydroxides and carbonates began to form. The leaching of uranium compounds, as well as fission and activation products, from the LFCM became possible.

Inclusions of chornobylite $(Zr_{1-x}U_x)SiO_4$ and metal globules did not undergo significant changes.

The synthesis of the mineral Weeksite $(K, Na)_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$ began after the accident. It could have begun after the formation of cracks through which water penetrated into the inclusions. It is possible that the synthesis of this compound occurred in several stages. This process is still ongoing.

We see that both processes – the oxidation of urania in inclusions and the synthesis of uranyl silicate hydrate $(K, Na)_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$ – influence each other. These processes result in an increase in the volume of the inclusions and, accordingly, in the formation of a large number of cracks.

The crystallization process of the amorphous $(Zr,U)O_x$ phase began during the accident. At that stage, it contained monoclinic and tetragonal zirconia ZrO_2. The crystallization process continued after the accident. In 2018, LFCM contained 1–2 wt.% cubic zirconium oxide ZrO_2 and 1–1.5 wt.% tetragonal zirconium oxide ZrO_2.

The glass-phase crystallization process began during the accident. It is still ongoing. This is indicated by the fact that the brown ceramics contain several phases of silicon oxide SiO_2, aluminosilicate Al_2SiO_5, and possibly calcium silicate Ca_2SiO_4.

We believe that the behavior of LFCM is determined not by several physicochemical processes individually, but by their mutual influence and interrelations. The accumulation of tracks enabled the formation of nanochannels and ensured the open porosity of the LFCM. Air penetration through nanochannels into the urania UO_x inclusions allowed further oxidation of urania in the inclusions, which, in turn, increased in volume and provoked the crack-formation process. The presence of cracks made it possible for water to penetrate into the urania UO_x inclusions and interact, together with dissolved salts and gases, with urania, forming soluble uranium compounds and hydrates. The synthesis of the $(K, Na)_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$ phase became possible after the accumulation of the sufficient concentration of radiation defects in the material. The presence of a significant concentration of radiation defects also stimulated the crystallization process.

2.4. Microstructure evolution model in 2016 and its update in 2021

2.4.1. Microstructure scheme of brown LFCM ceramics

For the first time, a model of the evolution of the LFCM microstructure was created in 2016 [9]. In 2021, the model was updated using the then-recent X-ray diffraction data on brown LFCM ceramics obtained in the period 2017–2020 [11]. Brown LFCM ceramics were a material consisting of a glass phase containing crystalline inclusions of urania, zirconia, chornobylite, *etc.* The glass phase was an "undercooked" glass with an uneven distribution of elements. The material contained gas pores, nanochannels, and cracks. Nanochannels and cracks penetrated the material and connected the gas pores with the external environment and with one another. Cracks and nanochannels are distributed unevenly throughout the LFCM. Their concentrations were high in the vicinity of crystalline inclusions of urania. The microstructure elements ranged in size from nanometers (the diameter of nanosized channels) to hundreds of microns (the length of cracks). We are therefore forced to present the microstructure of LFCM schematically. The microstructure of brown LFCM ceramics (2021 model) is shown in Fig. 1.

Inclusions of urania are represented by urania $UO_{2.34}$ (see Fig. 1). The zirconia inclusions contained uranium and had a cubic or tetragonal structure. We also see zirconium silicate inclusions known as Chornobylite $(Zr, U)SiO_4$. Potassium-sodium uranium silicate hydrate $(K, Na)_2(UO_2)_2(Si_2O_5)_3 \cdot 4H_2O$ (the mineral Weeksite), discovered in 2019, was most likely located in the contact zone between urania and the silicate-glass phase surrounding the urania UO_x inclusions. It was synthesized through the interaction of urania with potassium-, sodium-, and silicon-containing oxides from water and the LFCM glass phase.

Silicon oxides SiO_2 – trigonal, orthorhombic (1), orthorhombic (2), and, possibly, tetragonal – as well as aluminum silicate Al_2SiO_5 and, possibly, calcium silicate Ca_2SiO_4, are most likely located in the bulk of the silicate glass phase of brown LFCM ceramics (see Fig. 1).

2.4.2. Stages of microstructure evolution according to the LFCM microstructure evolution model for 2016–2021

In the 2016 model of LFCM microstructure evolution, the following stages of evolution of the LFCM bulk microstructure, as well as their sequence and duration, were identified [9].

Data on the phase composition of brown LFCM ceramics obtained in the period 2016–2020, made it possible to identify two additional stages in the evolution of the internal LFCM microstructure [11].

2.5. Newly discovered (2021–2023) physicochemical processes that predetermine the microstructure of LFCM

Our new data (2022–2023) on black LFCM ceramics [12] showed that after the accident, the microstructure of LFCM was formed under the influence of radiation-stimulated formation of the phases Rameauite $K_2Ca[(UO_2)_3O_3(OH)_2]_2 \cdot 6H_2O$ and Katoite $Ca_{2.916}Al_2(SiO_4)_{1.104}(O_4H_4)_{1.89}$, as well as the crystallization of calcium-magnesium silicate $CaMgSiO_4$, magnesium aluminate (spinel) $MgAl_2O_4$, and magnesium silicates $MgSiO_3$ and Mg_2SiO_4. The synthesis of Rameauite $K_2Ca[(UO_2)_3O_3(OH)_2]_2 \cdot 6H_2O$ as a uranium-containing phase should be attributed to processes of group No. 7. Data on the crystallization of magnesium silicates $MgSiO_3$ and Mg_2SiO_4, magnesium aluminate (spinel) $MgAl_2O_4$, and calcium-magnesium silicate $CaMgSiO_4$, will complement the information on the glass-phase crystallization process (process No. 8). The synthesis of Katoite $Ca_{2.916}Al_2(SiO_4)_{1.104}(O_4H_4)_{1.89}$ as a non-uranium phase should be attributed to a new group of processes involving the interaction of water and dissolved gases and salts with LFCM, as well as the synthesis of soluble and hydrated non-uranium compounds (process group No. 9).

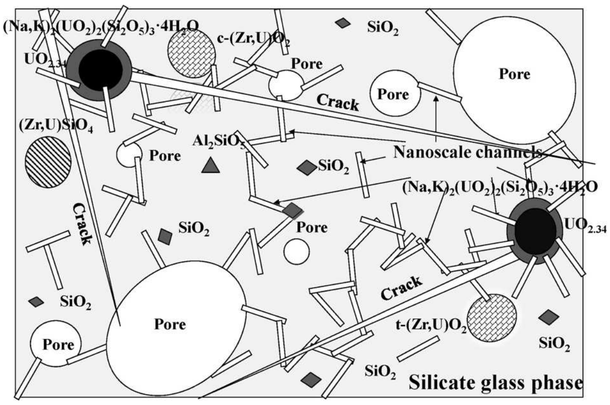

Fig. 1. Brown ceramics microstructure (schematic representation) [11]

3. Results

3.1. Sequence and relationship of previously known (2016–2020) and newly discovered (2021–2023) physicochemical processes

Let us take a closer look at the processes in black LFCM ceramics discovered in 2021–2023.

Radiation-stimulated synthesis of the Rameauite $K_2Ca[(UO_2)_3O_3(OH)_2]_2 \cdot 6H_2O$ phase in black ceramics apparently occurred after the oxidation of most of the urania in the inclusions to UO_3 (process No. 3). This became possible owing to the penetration of atmospheric oxygen into these urania inclusions through cracks from the external environment (process No. 2). The formation of the Rameauite phase occurred when water entered the urania inclusions (process No. 5). Atmospheric oxygen and water penetrate into the urania inclusions through cracks formed due to an increase in the volume of these inclusions (process No. 4). An increase in the volume of inclusions (process No. 3) occurred during the oxidation of urania due to oxygen entering through

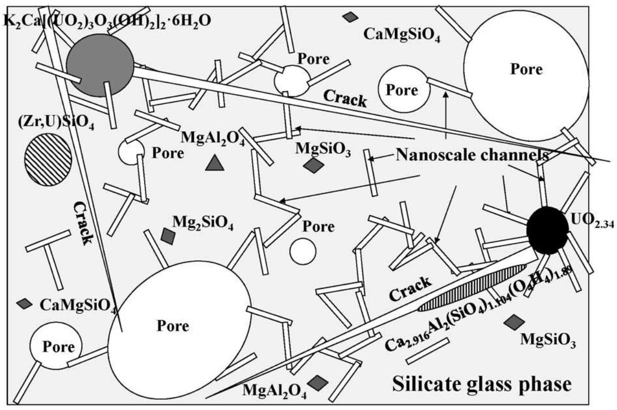

Fig. 2. Black ceramics microstructure taking into account new data (schematic representation)

nano-sized pore channels. The nanosized pore channels are formed by the interconnection of some α-particle tracks generated through process No. 1.

Crystallization of magnesium silicates $MgSiO_3$ and Mg_2SiO_4, magnesium aluminate (spinel) $MgAl_2O_4$, and calcium-magnesium silicate $CaMgSiO_4$ took place during the accident owing to the cooling of the melt, continued over the 38 years following the accident, and is still ongoing. After the accident, the crystallization process was stimulated by self-irradiation of LFCM.

The synthesis of Katoite $Ca_{2.916}Al_2(SiO_4)_{1.104}(O_4H_4)_{1.89}$ became possible owing to the penetration of water (process No. 5) into the glass phase through cracks (process No. 4) formed as a result of the oxidation of urania (process No. 3) in its inclusions. The oxidation of urania occurred owing to the penetration of atmospheric oxygen (process No. 2) through nanochannels into the LFCM. They were formed owing to the interconnection of some tracks of α-particles generated during α-decays of radionuclides (process No. 1).

Data on the phase composition of black ceramics allow us to divide the physicochemical processes described in the previous section into two groups.

Processes No. 1–5 and 7 took place sequentially one after another. They led to changes in the phase composition of LFCM, oxidation of urania, synthesis of Rameauite $K_2Ca[(UO_2)_3O_3(OH)_2]_2 \cdot 6H_2O$, as well as changes in the structure of LFCM, and the formation of nanosized pore channels and cracks. Although the formation of nanosized pore channels may continue, the oxidation of urania and its interaction with water to form Rameauite (containing U in its highest oxidation state U(VI)) is almost complete.

The crystallization of the silicate-glass phase (process No. 8) began earlier and now proceeds independently in parallel with processes No. 1–5 and 7. Now the glass-phase crystallization is at the initial stage. The total content of crystalline phases formed during the crystallization process does not exceed 4 wt.%.

3.2. Augmented model of the evolution of the LFCM microstructure (for 2025 year)

3.2.1. Microstructure scheme of black LFCM ceramics

The microstructure of black LFCM ceramics, taking into account new data for 2021–2023, is shown schematically in Fig. 2. Black LFCM ceramics are materials similar to brown ceramics. They also consist of a glass phase containing inclusions of crystalline phases. The glass phase has an uneven distribution of elements. It is an “undercooked” glass. Black ceramics also contain gas pores, nanochannels and cracks. Just as in brown ceramics, nanochannels and cracks penetrated the material and connected gas pores with the external environment and with one another. Cracks and nanochannels are distributed unevenly throughout the LFCM.

Uranium-containing crystalline inclusions in black ceramics (80–90%) are in the form of Rameauite $K_2Ca[(UO_2)_3O_3(OH)_2]_2 \cdot 6H_2O$, a significantly smaller part (10–20%) is in the form of urania $UO_{2.338}(U_4O_9)$ and a small part (up to 1%) – in the form of chornobylite $Zr_{1-x}U_xSiO_4$.

Katoite $Ca_{2.916}Al_2(SiO_4)_{1.104}(O_4H_4)_{1.89}$ is most likely located on the surfaces of cracks within the glass phase.

Magnesium silicates Mg_2SiO_4 and $MgSiO_3$, magnesium aluminate (spinel) $MgAl_2O_4$ and calcium-magnesium silicate $CaMgSiO_4$ are apparently located within the bulk of the glass phase.

3.2.2. New stages in the evolution of the LFCM microstructure; duration of stages (model 2025)

Data on the phase composition of black LFCM ceramics obtained in the period 2020–2023 [12] necessitated a revision of stages 4, 5, and 6. It is necessary to take into account that stage 5 of the synthesis of uranyl silicate sodium-potassium hydrate $(\mathrm{Na,K})_2(\mathrm{UO}_2)_2(\mathrm{Si}_2\mathrm{O}_5)_3\cdot 4\mathrm{H}_2\mathrm{O}$ is essentially included in stage 4 (Water penetration through cracks into LFCM. Urania interacts with water in the inclusions). Stage 5 should be associated with the interaction of water with non-uranium phases of LFCM.

Stages 4, 5 and 6 in the new version are:

4. Water penetration through cracks into LFCM. Water interacts with urania in the inclusions. Synthesis of uranium oxyhydroxides.

5. Water penetration through cracks into LFCM. Its interaction with phases that do not contain uranium. Synthesis of oxyhydroxides that do not contain uranium.

6. Crystallization of amorphous phases: silicate-glass phase and amorphous phase $(\mathrm{Zr,U})\mathrm{O}_x$.

Now we will focus on the duration and sequence of the above stages:

Stage 1 (nanochannel & open porosity creation) started after the accident; its duration is up to 12 years. This stage has ended for brown and black ceramics.

Stage 2 (air penetration, UO_x oxidation expansion) began during the accident and continued after the accident (1996–1998) after the formation of open porosity. In brown ceramics, stage 2 (UO_x inclusion oxidation) is currently ongoing; in black ceramics it is almost complete. The duration of this stage in black ceramics is up to 2 decades, whereas in brown ceramics it is up to 3 decades. The stage will be completed with the oxidation of urania to UO_3.

Stage 3 (formation of cracks at inclusions) began some time after the start of stage 2 of oxidation of urania in inclusions. Stage 3 continues in brown ceramics, and is nearing completion in black ceramics. The duration of the stage in black ceramics is up to 2 decades, whereas in brown ceramics it is up to 3 decades.

Stages 1 and 2, 2 and 3 are likely to overlap each other.

Stage 4 began after the formation of cracks (from 2004 to 2011). After the completion of the confinement complex and the Shelter object, this stage still continues. The penetration of water into LFCM in the form of atmospheric precipitation has stopped, but continues in the form of vapor in the air. Stage 4 processes have slowed down significantly. The duration of this stage is 3–4 decades.

Stage 5 began after the formation of cracks (from 2004 to 2011). At the moment it is not expected to be active in brown ceramics, but in black ceramics it is. Since 2018 and the completion of the confinement complex and the Shelter object the penetration of water via atmospheric precipitation has stopped, but continues in the form of vapor in the air. Stage 5 processes are currently inactive; the duration of the stage is 3–4 decades.

Stage 6 started during the accident during the lava melt cooling, continued throughout the 39 years after the accident, and continues today. The stage duration can be up to 6–8 decades (before the amorphous phase $(\mathrm{Zr,U})\mathrm{O}_x$ and the main part of the glass phase is transformed to the crystalline state).

Thus, brown LFCM ceramics are currently at stages 2, 3, 4 and 6, black ceramics at stages 4, 5, and 6.

3.3. Supplemented forecast of the state and behavior of LFCM according to the 2025 model

The augmented model of microstructure evolution allows us to supplement the forecast of LFCM behavior for the near and distant future. We take into account both new data on black ceramics and data on brown ceramics obtained earlier. Let us look at it in more detail.

Self-irradiation of LFCM will continue (including α-decay of radionuclides). Black LFCM ceramics (just like brown) have open porosity, which was formed due to the fact that nanosized pore channels connected gas pores with the external environment (process No. 1). It no longer matters, whether the number of nanochannels in black and brown LFCM ceramics will increase. Nanochannels have played their role. They have provided the penetration of air oxygen into urania inclusions (process No. 2).

The process of oxidation of urania UO_x in inclusions (process No. 3) will continue to a greater extent in brown ceramics, to a lesser extent in black ones.

The volume of cracks, their length and, possibly, their number will increase due to an increase in the volume of urania inclusions, more significantly in brown ceramics, less significantly in black (process No. 4). The cracks played a significant role; they allowed water to penetrate into the urania inclusions.

Water penetration into LFCM through cracks into urania inclusions (process No. 5) under the conditions of the confinement complex and the Shelter object has slowed down significantly. The flow of water in the form of precipitation has completely stopped, but the flow of water in the form of vapor in the air will continue. The interaction of water with urania UO_x and the synthesis of soluble uranium and hydrated compounds in brown ceramics have slowed down, and in black ceramics it has practically ceased (process No. 7).

Crystallization of the silicate-glass phase (process No. 8) will continue in both brown and black ceramics, as well as the possible crystallization of the amorphous (Zr, U)O_x in brown ceramics.

The synthesis of uranium-free hydrated compounds (process No. 9) in black ceramics will slowly continue; in brown ceramics, the development of this process may begin.

Processes No. 1–5 and 7 took place sequentially one after another. One process created the conditions for the next. The interconnection of at least some tracks of α-particles formed during α-decays of radionuclides "switched on" this group of processes. These processes significantly changed the structure of LFCM. Nanosized channels and cracks were formed. The mechanical characteristics of LFCM have deteriorated significantly. The confinement complex and the Shelter object, built over the 4th unit of the ChNPP, did not stop the oxidation process of urania (process No. 3), but significantly slowed down the penetration of water into LFCM (process No. 5) and, accordingly, the interaction of water with urania.We see that the urania oxidation and the synthesis of Rameauite are almost complete. Therefore, in the future, this group of processes will no longer significantly affect the structure of black LFCM ceramics.

Data on the phase composition of black ceramics allow us to adjust the forecast of the behavior of brown ceramics, which was made in 2021 [12]. We predicted that the process of oxidation of urania to UO_3 and the subsequent synthesis of uranyl silicate sodium-potassium hydrate $(\mathrm{Na,K})_2(\mathrm{UO}_2)_2(\mathrm{Si}_2\mathrm{O}_5)_3\cdot 4H_2O$ will cause an increase in the volume of inclusions and destruction of brown LFCM ceramics. However, the oxidation of urania to UO_3 and the subsequent synthesis of Rameauite $\mathrm{K_2Ca[(UO_2)_3O_3(OH)_2]_2\cdot 6H_2O}$ in black LFCM ceramics did not lead to destruction of the sample. Apparently, even such a significant increase in the volume of inclusions of uranium-containing phases may not lead to the destruction of the material. It is possible that some of the urania and/or mineral-like uranium compounds are released from the inclusions into the cracks.

But the crystallization process (process No. 8) has occurred in the past, is ongoing, and will continue in the future regardless of the penetration of air oxygen and water (or its vapor) into the LFCM. The confinement complex and the Shelter object will not affect crystallization of the LFCM glass phase. The driving force for crystallization is a decrease in the free energy of the glass (amorphous) substance. The crystallization process of the LFCM glass phase is practically independent of environmental conditions. The crystallization process will lead to changes in the phase composition of the lava (formation of crystalline phases in the glass phase), changes in the volume of part of the material, an increase in mechanical stress, the formation of cracks near the crystalline phases, and ultimately the possible destruction of the LFCM.

The crystallization process will determine the behavior of LFCM in the next few decades. In the future, it will be necessary to pay much more attention to this process.

The crystalline-phase content in black ceramics is close to that in brown ceramics. In black ceramics, crystallization is also at an early stage. Therefore, a forecast of the time to reach the stage of rapid (or avalanche-type) crystallization (by 2032–2039) is relevant [12]. The appearance of a significant number of crystalline nuclei and their relatively rapid growth will lead to a decrease in volume at the sites of formation of crystalline phases. This will lead to the emergence and growth of mechanical stress in the glass phase. Exceeding the limits of mechanical stress after some time will cause the destruction of a significant part of the glass phase into particles with an average size of 20–50 μm. A range of glass phase particle sizes from 10 to 120 μm is possible.

We must take into account that crystallization of the glass phase is multiphase. The rates of nucleation and growth rates of crystals for all these phases are different. One of these phases (or several of them) will crystallize faster, their content will increase faster. Due to this, the elemental composition of the remaining glass phase will change, which will cause changes in both the growth rates and the nucleation rates of crystals. Crystallization of several phases complicates predictions of the behavior of the glass phase during further crystallization. Most likely, the crystallization of several phases will slow the overall crystallization of the glass phase.

4. Discussion

Our data [10, 12] indicate that black and brown LFCM ceramics contain 10 and 9 crystalline phases, respectively. The crystalline phases are embedded in the silicate glass phase. The content of a significant portion of these phases (9 and 8 phases, respectively) is no more than a few percent by weight. We believe that, given the above data, brown and black LFCM ceramics can be classified as multiphase materials with a low content of crystalline phases.

It should be noted that almost all data on the phase composition of LFCMs obtained by various authors over a fairly long period of time (from 1994 to 2024) fit well within the general understanding of the evolution of the microstructure of these materials. However, the results presented in [19] are an exception. The authors provided photographs of polished LFCM sections and showed the presence of urania with zirconium, $UO_x + Zr$. The authors do not provide data on other phases, such as uranium oxyhydroxides, i.e. phases that result from the oxidation of urania and subsequent interaction with water, although, judging by the publication date (2023), the samples had been kept under laboratory conditions for more than 30 years. We can assume that the LFCM samples were apparently stored in hermetically sealed packaging or in the form of sections embedded in an air- and water-vapor-impermeable medium, such as epoxy resin.

We believe that attention should be paid to the data obtained for simulant LFCM [20–22]. Analysis of the results shows that our colleagues not only correctly selected the composition of the initial mixture of components, but also successfully chose the conditions for obtaining simulant brown and black ceramics. Their results confirmed not only the formation of crystalline phases of urania UO_2 and zirconium-containing urania ($UO_x + Zr$), cubic zirconia with uranium $(Zr_{1-x}, U_x)O_2$, monoclinic zirconia ZrO_2, and chornobylite $(Zr_{1-x}, U_x)SiO_4$, but also the formation of sodium aluminosilicate, albite ($NaAlSi_3O_8$). If the phases of urania, zirconia, and chornobylite $(Zr_{1-x}, U_x)SiO_4$ are the result of long-recognized physicochemical processes, then the formation of albite ($NaAlSi_3O_8$) confirms the crystallization of the silicate melt (the precursor of the silicate glass phase) during cooling in the furnace.

In the period following the accident, as a result of a number of physicochemical processes associated with urania inclusions (processes No. 1–5 and 7), cracks formed in significant quantities in LFCM. This led not only to a significant deterioration of the mechanical properties, but also to the destruction of part of the LFCM and the formation of aerosols. If we now extract LFCM from the confinement complex and the Shelter object, we will inevitably encounter great difficulties due to the formation of a significant amount of aerosols. The crystallization process of the LFCM glass phase will continue to develop in the future. It will lead to the formation of even more cracks in the LFCM. Extracting LFCM in the future will inevitably lead to even greater difficulties, more aerosols, and even smaller particle sizes. Unfortunately, with time, the difficulties of extracting LFCM materials will only increase.

LFCM of the Chornobyl reactor must be conditioned into a safe state and transferred to secure storage. At present, LFCM are not materials capable of retaining radionuclides. LFCM contain nano-sized pore channels and cracks. Urania and uranium-containing compounds in inclusions are not corrosion-resistant. Experts are increasingly recognizing the need to develop technologies for these materials, in particular solid-phase conditioning methods. It is necessary to ensure that LFCM are the first barrier preventing radionuclide release into the environment. In the course of studying LFCMs and predicting their evolution, specialists have accumulated considerable experience in working with them. The microstructure of LFCM also suggests possible approaches for their management.

Previously, we showed [15] that heat treatment of LFCM leads to the complete closure of nano-sized pore channels (at 150–400 °C) and cracks (at 200–530 °C). Thus, the pore space closes, the surface area decreases. Heat treatment at these and higher temperatures can lead to the thermal decomposition of uranium oxyhydroxides and carbonates.

The use of electrochemical methods [26] can promote the redistribution of uranium compounds in the pore space of LFCM (in pores and cracks), which will facilitate the synthesis of corrosion-resistant uranium compounds during subsequent heat treatment at lower temperatures and with shorter processing times.

Our works show [10, 12] that the LFCM glass phase crystallizes, i.e. the material tends to transition to a thermodynamically more stable state. To facilitate this process, it is advisable to carry out controlled crystallization of the LFCM glass phase by heat treating these materials. Thus, we will be able to control crystalline nucleation sites and achieve controlled crystal growth. Appropriate selection of parameters will prevent the destruction of LFCM due to activation of the sintering process of an already partially crystalline material. We will also be able, if possible, to select the phases required for crystallization and implement the necessary sequence of their formation. It is important to select crystalline phases capable of retaining radionuclides within their crystal lattice. Particular attention should be paid to the radionuclides of uranium, plutonium, and americium.

We believe that future management of LFCM will require the application of concepts and knowledge related to glass [27] and crystalline materials [28], which are regarded as materials for radionuclide immobilization. Data on the crystallization process of the LFCM glass phase create the prerequisites for classifying LFCM as glass-crystalline materials. Some crystalline phases may serve as a matrix (the first barrier) for radionuclides, whereas the remaining crystalline phases together with the glass phase may constitute the second barrier. For this purpose, it is advisable to use existing knowledge and experience in converting glass into glass ceramics [29, 30].

5. Conclusions

The microstructure evolution model of the Chornobyl lavas has been supplemented using new data on black ceramics. Of the nine previously known physicochemical processes, three were once again confirmed: oxidation, radiation-stimulated phase formation, and crystallization, which were first identified in the study of brown ceramics. A new process has been discovered – the interaction of water with the glass phase of LFCM accompanied by the synthesis of hydrates of non-uranium compounds. The oxidation process of urania UO_x in inclusions has been further clarified. The durations of the stages of microstructure evolution have been revised.

In the future, a group of processes in LFCM (formation of open nanochannels due to the merging of some α-particle tracks; penetration of atmospheric oxygen into LFCM and urania inclusions through these open channels; oxidation of urania in inclusions by atmospheric oxygen; penetration of water into LFCM through these cracks; formation of cracks due to the expansion of oxidised urania inclusions; interaction of urania with water, salts, and gases dissolved in it; synthesis of hydrates and soluble uranium compounds) will no longer significantly affect the structure of black LFCM ceramics. An increase in the volume of urania inclusions due to oxidation and the synthesis of mineral-like uranium compounds is unlikely to lead to the destruction of LFCM.

There will be little or no destruction of LFCM in the coming years. It has been confirmed that the crystallization process (i.e. crystallization of a single phase) may approach an avalanche stage by 2032–2039 (in 8–15 years). A significant portion of the glass phase may disintegrate into particles with an average size of 20–50 μm (within the size range from 10 to 120 μm). Crystallization of multiple phases makes it difficult to predict the behavior of the glass phase. Most likely, the formation of several crystalline phases will slow down the crystallization process of the glass phase as a whole.

In the long term, the behavior of LFCM (both brown and black ceramics) will be determined by the crystallization process of the silicate glass phase.

Technological and methodological approaches to the development of LFCM management methods have been proposed. Heat treatment of LFCM makes it possible to completely close nano-sized pore channels and cracks, carry out the thermal decomposition of hydrated uranium compounds, and synthesize corrosion-resistant anhydrous uranium compounds. Uranium compounds in the pore space of LFCM (in pores and cracks) can be redistributed as a result of electrochemical treatment. Controlled crystallization of the glass phase will facilitate the transformation of LFCM into a thermodynamically stable state.

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ДОПОВНЕНА МОДЕЛЬ ЕВОЛЮЦІЇ МІКРОСТРУКТУРИ ЧОРНОБИЛЬСЬКИХ ЛАВ

Модель еволюції мікроструктури Чорнобильських “лав” (або лавоподібних паливовмісних матеріалів, ЛПВМ) 4-го блоку Чорнобильської АЕС оновлено з урахуванням нових даних стосовно чорної кераміки. На цей момент ЛПВМ є багатофазними матеріалами: включення кристалічних фаз (які містять і не містять уран) перебувають у силікатній склофазі, яка містить газові пори, тріщини й нанорозмірні порові канали. ЛПВМ мають відкриту пористість. Підтверджено й уточнено параметри трьох із дев’яти відомих раніше фізичних і хімічних процесів, які відбуваються у коричневій кераміці: окислення, радіаційностимульоване фазоутворення й кристалізація. Ідентифіковано ще один новий хімічний процес – синтез оксигідроксиду, який не містить урану. Додано нову стадію еволюції мікроструктури. Переглянуто тривалості стадій. Надано оновлений прогноз стану й поведінки ЛПВМ. У майбутньому група фізичних і хімічних процесів, які послідовно відбуваються один за одним у коричневій кераміці й стосуються включень оксиду урану, вже не буде істотно впливати на мікроструктуру чорної кераміки. У найближчі роки руйнування ЛПВМ буде малим або зовсім не буде. Підтверджено, що в середньостроковій перспективі можливе руйнування ЛПВМ, підтверджено його терміни й розміри частинок, які можуть утворитися в результаті руйнування ЛПВМ. У віддаленій перспективі поведінка ЛПВМ (як коричневої, так і чорної кераміки) буде визначатися процесом кристалізації силікатної склофази. Кристалізація кількох кристалічних фаз вірогідніше всього буде сповільнювати кристалізацію склофази в цілому. Розглянуто методичні й технологічні підходи до поводження з ЛПВМ.

Ключовіслова: лавоподібні паливовмісні матеріали, модель еволюції, мікроструктура, фізичні та хімічні процеси, прогноз, кристалізація, радіаційно-стимульоване фазоутворення, окислення, комплекс конфайнмента й об’єкта “Укриття”, методичні та технологічні підходи.