Synthetic Fluorphlogopite – Refractory Material for Electrolysers in Non-ferrous Metallurgy

A. M. Ignatova, M. N. Ignatov

Synthetic fluorphlogopite is a refractory material for non-ferrous metallurgy, produced by casting can preserve its integrity after 200 cyclic temperature changes from 800 to 20 °C by cooling in water. This material has long product life with absence of surface phenomena associated with the Rehbinder effect. The paper describes the structure of this material and its behavior in the process of work. On basis of this knowledge the author presents a method of the synthesis of new refractory materials from technogenic silicate materials.

1 Introduction

The non-ferrous metallurgy industry is a large consumer of refractory materials. Approximately 120 000 t of corundum refractories are used in electrolysers for magnesium and aluminium per year. The main issues by using corundum include a short product life and decreased energy efficiency. Consequently, new approaches to search for materials to replace corundum in electrolysers are needed.

Fig. 1 The structure of synthetic fluorphlogopite using an optical polarization microscopy (×150)

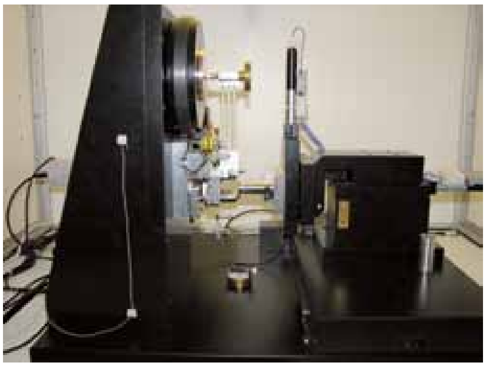

Fig. 2 The NanoTest 600

Synthetic fluorphlogopite is a material that can increase the efficiency of the electrolyser and has a longer product life. Synthetic fluorphlogopite is similar to the European material Macor, but it has significant differences in composition; synthetic fluorphlogopite is made of silica sand, alumina, magnesia, and potassium silicofluoride.

Synthetic fluorphlogopite ($[KMg_3(AlSi_3O_{10})F_2]$ – which will hereafter be referred to as fluorphlogopite) has a density of 2,52 g/cm^3, a low-temperature (25 – 300 °C) thermal expansion of 9,7 × 10^{-6} m/(m·K) and resistance to cyclic temperature changes. This material can preserve its integrity after 200 cyclic temperature changes from 800 to 20 °C by cooling in water. This material is produced by casting (like production of EUTIT). It contains the typical structural parts in the following concentrations: potassium fluorphlogopite (80 – 90 %), accessory elements (5 – 7 %) and glass phase (2 – 8 %) [1, 2]. The microstructure of the material is depicted in Fig. 1.

Anna M. Ignatova, Mikhail N. Ignatov
Perm 614000, Russia

Corresponding author: *A.M. Ignatova*
E-mail: *iampstu@gmail.com*

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The reason for the long product life of fluorphlogopite is the absence of surface phenomena associated with the Rehbinder effect. A more thorough study of this phenomenon should be performed.

The aim of this study is to analyse the distinctive features of fluorphlogopite and its behaviour under operating conditions.

2 Experiments

The behaviour of fluorphlogopite under load was studied by nanoindentation. The NanoTest 600 equipment (Micro Materials Ltd./GB, Fig. 2) [3] was used.

3 Results

All the indentation tests were performed using the continuous stiffness measurement (CSM) method with a frequency of 200 Hz and displacement amplitude of 2 nm. A Berkovich indenter was used. The indentation depth is calculated by including the defect tip (i.e., the missing end of the tip compared to a perfect Berkovich geometry) [6]. Indentations were made on all surfaces of the plot under investigation with 40 mkm steps.

In the structure of fluorphlogopite, two separate zones with different hardness values were found: first zone –1 GPa, second zone –0,45 GPa, and different Young's modulus: first zone –18 GPa, second zone –50 GPa. The distribution of the hardness values on the surface of fluorphlogopite on a plot 360 mkm × 360 mkm is shown in Fig. 3a.

After identifying the hardness, the authors scratched this part of surface with a force

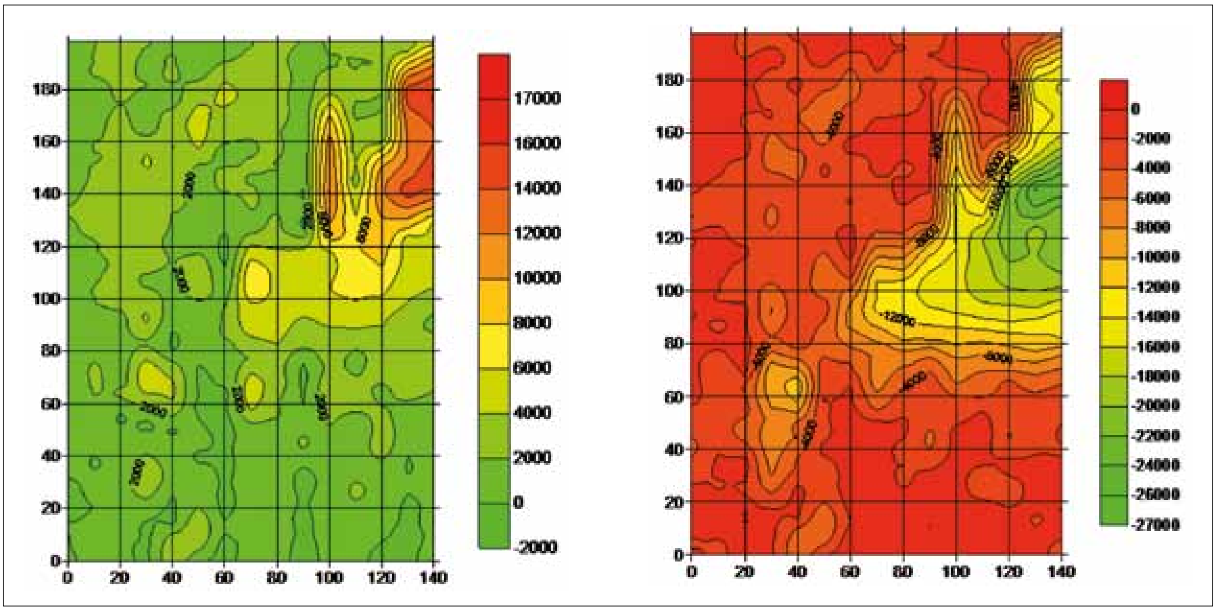

Fig. 3a–b Distribution of the hardness values on the surface of fluorphlogopite on a plot 360 mkm **×** **360** mkm**: a – before scratching, b – after scratching**

Tab. 1 Composition of the basic material for the samples

Concentration [%]									
SiO_2	Al_2O_3	CaO	FeO	MgO	Fe_2O_3	TiO_2	K_2O+Na_2O	Cr_2O_3	Loss
44–49	9–20	6–16	5–13	5–13	2–7	0,5–2,5	1–5	0,2–0,7	~2

equal to 200 mN to imitate the fluorphlogopite behaviour in the electrolysis condition. Changes in the distribution of the hardness values on the surface of fluorphlogopite after scratching are demonstrated in Fig. 3b.

The results of nanoindentation were compared with the data of the microstructure and these results in terms of an anisotropic structure (structure composed of layers) were generalized. This enables a qualitative evaluation of the refractory resistivity under the aggressive condition of electrolysis.

4 Discussion

The structural peculiarities of the material influence the hardness value because the hardness depends on the strength of the chemical bond between separate silicon-oxygen tetrahedra. The part of microstructure that has a hardness value of 0,45 GPa consists of silicates with single and double chains and a high concentration of Na_2O and MgO. Another part of it with a hardness value of 0,45 GPa consists of sheets of silicates and contains a high concentration of Al_2O_3 and TiO_2. The high hardness value is connected with the isomorphism displacement in the silicon-oxygen tetrahedra between SiO_2 and Al_2O_3. While deforming fluorphlogopite, a silicon-oxygen tetrahedra turns, thus changing the appearance and causing cracks to grow between two separate parts of structure [4].

However, cracks do not appear in fluorphlogopite. A structural study using X-rays shows that in its structure there is a part with a high concentration of fluorine. The link between oxygen and fluorine is very strong, even stronger than the link between silicon and oxygen. The analysis of the experimental data shows that fluorine ions form a layer, which connects single and double chains and sheet silicates like a bridge (Fig. 4).

The absence of destruction on the fluorphlogopite surface cannot be explained by just the strong link fluorine creates with the layers of silicates. The links through fluorine are similar to a flexible bridge, so the Rehbinder effect does not appear [5, 6].

It was decided to check this theory with experiments with a composition used for stone casting (like basalt cast Fig. 5). A raw composition like basalt casting was used (Tab. 1) and by adding different reagents with fluorine in different concentration (Tab. 2) a

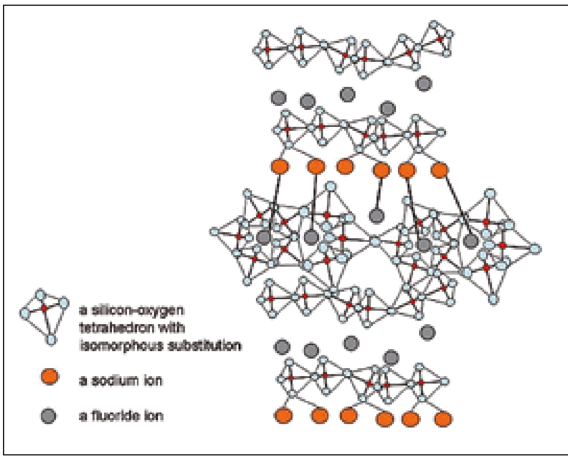

Fig. 4 **A model of the structure of synthetic fluorphlogopite**

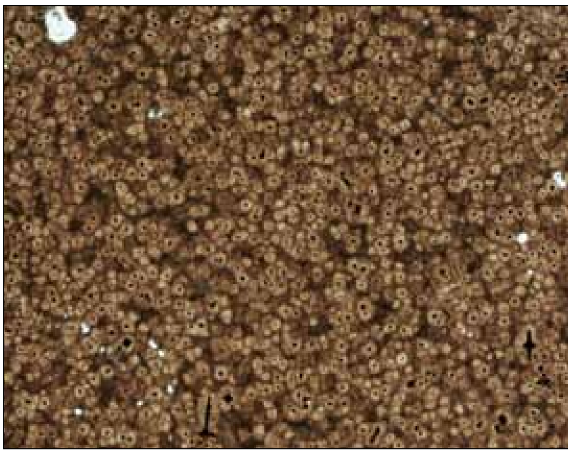

Fig. 5 **The structure of the basic material without additives using optic polarization microscopy (×** **100)**

Fig. 6 The structure of samples with additives using an optical polarization microscopy: a – SH 3 (× 100); b – SH 4 (× 200)

Tab. 2 Composition of the samples

Sample	Composition
SH1	5 % potassium silicofluoride; 95 % basic material
SH 2	10 % potassium silicofluoride; 90 % basic material
SH 3	20 % potassium silicofluoride; 80 % basic material
SH 4	5 % ammonium fluorosilicate; 95 % basic material
SH 5	10 % ammonium fluorosilicate; 90 % basic material
SH 6	20 % ammonium fluorosilicate; 80 % basic material
SH 7	5 % sodium silicofluoride; 95 % basic material
SH 8	10 % sodium silicofluoride; 90 % basic material
SH 9	20 % sodium silicofluoride; 80 % basic material

casting material was made. After that, the macrostructure was observed with an optical polarization microscope. The samples SH 3 (20 % potassium silicofluoride; 80 % basic material) and SH 4 (5 % ammonium fluorosilicate; 95 % basic material) showed that there are sheet structures similar to synthetic fluorphlogopite (Fig. 6).

This discussion of the present findings has confirmed the data accumulated in earlier studies. The study demonstrates that fluorine addition in stone casting can make a radical change in the structure and properties of this material.

5 Conclusion

Fluorine is the most important component in casting refractory materials for the non-ferrous metallurgy. These data will be used in the work for the synthesis of new refractory materials.

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