

# High-power nanosecond electromagnetic pulses and dielectric barrier discharge in air consequences on structural and structure sensitive properties of ilmenite surface

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**Abstract.** The paper presents the results of experimental studies on the influence of two types of nonequilibrium electrical discharges (high-power nanosecond electromagnetic pulse (HPEMP) and dielectric barrier discharges (DBD) in air at atmospheric pressure) have on the surface morphology, microhardness, and physicochemical properties of natural ilmenite (Juina deposit of Brazil). Scanning electron microscopy (SEM–EDX), Fourier-transform infrared spectroscopy (FTIR), microhardness testing, contact angles of surface wetting, and streaming potentials are used to examine the morphology, defects, chemical composition of ilmenite surfaces, and its structure sensitive properties. Using FTIR, we established, the following possible mechanisms of the nonthermal effect of HPEMP and DBD low temperature plasma irradiation, which modify the structural state of ilmenite surfaces: (i) the transformation (destruction) of the mineral's crystalline structure; (ii) the electrical disintegration and removal of fine films of iron oxides (hydroxides) from the ilmenite surfaces, and (iii) the subsequent hydroxylation and/or oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  iron ions on the surfaces, due to the effect of the products of microdischarge plasmas. Advantages of using brief energy treatments ( $t_{\text{treat}} = 10\text{--}30$  s) to modify the structural-chemical state of ilmenite surfaces and the physicochemical properties of mineral in order to improve the efficiency of processing complex titanium ores are shown.

**Keywords:** ilmenite, high-power nanosecond electromagnetic pulses, dielectric barrier discharge, surface, microscopy, spectroscopy, microhardness, electrokinetic potential, contact angle.

## 1. Introduction

Ilmenite ( $\text{FeTiO}_3$ ) and rutile ( $\text{TiO}_2$ ) are the main minerals for the production of titanium and titanium dioxide. The content of titanium dioxide is more than 91% in rutilites and 42–62% in ilmenites [1]. Ilmenite raw material contains more than 82% of the world reserves of titanium required for the production of synthetic rutile ( $\text{TiO}_2$ , 95–98%) and titanium slag (70–85%), with the subsequent production of pigment titanium dioxide, Ti itself, and other products that employ them [1, 2]. Ilmenite concentrates that are ~55% and 44–49%  $\text{TiO}_2$  are obtained from present-day placers and ledge ores, respectively. Ilmenite–titanium magnetite ledge ores are enriched according to a gravitation magnetic method (scheme) with a yield of high-quality ilmenite concentrate (titanium dioxide,  $\text{TiO}_2$ , 45–52%), and titanium–magnetite vanadium-containing concentrate [3]. The use of the flotation process in enriching complex titanium ores allows us to reduce the losses of finely impregnated ilmenite and improve the quality of ilmenite concentrates [4].

Reduction melting is used in Russia to process ilmenite concentrates [1–3]. Preliminary mechanoactivation is employed to intensify the subsequent hydrochloric decomposition of Ti-containing concentrates [2], and for the UHF processing of rocks and concentrates to improve the efficiency of ilmenite floatation [5, 6]. The flotation tests [6] results revealed that, under the optimum microwave pretreatment conditions of mineral powdered sampling probes (2.45-GHz microwave oven MCR-3, rated power 800 W,  $t_{\text{treat}} = 450$  s), microwave irradiation has a remarkable effect on the flotation of ilmenite but no significant effect on the floatability of titanite at pH 6.0. The FTIR spectra and electrokinetic potential values were indicated that microwave irradiation can enhance the chemical adsorption of oleate ions (flotation reagent) on the surface of the ilmenite. After microwave irradiation, the effects of both the dissolution of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions and the oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ , the floatability of ilmenite was significantly improved, whereas that of titanite was not changed significantly [6].

Currently in Russia and the world, application of energy-saving high-voltage electric discharge technologies [7–14] in the processing of rebellious ores allows achieving effective disintegration of fine disseminated mineral complexes and creating optimal conditions to enhance the contrast of the physicochemical and flotation properties of minerals and subsequent separation during flotation due to the appearance of hydrophobic and hydrophilic nanoformations on their surface. This paper presents the results of experimental studies on the influence of two types of nonequilibrium electrical discharges (high-power nanosecond electromagnetic pulse (HPEMP [7]) and dielectric barrier discharges (DBD [15]) in air at atmospheric pressure) have on the surface morphology, microhardness, and physicochemical properties of natural ilmenite (Juina deposit of Brazil).

## 2. Experimental

### 2.1. Mineral samples

We used in our experiments the ilmenite (Fe,Mg)TiO<sub>3</sub> grains extracted from a sample of stream sediment (Juina, Brazil). The ilmenite samples were represented by individual grains 1–4 mm in size and specially prepared plane-parallel polished sections ~4.5 mm in thick.

The elemental composition of the ilmenite samples were determined via scanning electron microscopy and energy-dispersive X-ray microanalysis (SEM-EDX, semiquantitative analysis); the elemental composition of ilmenite was (wt %): Fe – 26.7, Mg – 3.2, Ti – 25.9, O – 38.7, C – 4.0, Cr – 1.0, Mn – 0.30, and Al – 0.2. Electron-microprobe analysis on a Cameca SX 100 microanalyzer were also used. According to the electron-microprobe analysis the chemical (elemental) composition and the contents of main impurities in the ilmenite samples was (wt %): TiO<sub>2</sub> – 56.18, FeO – 37.22, MnO – 1.14, MgO – 0.06, V<sub>2</sub>O<sub>3</sub> – 0.28, SiO<sub>2</sub> – 0.04, CaO – 0.04, Na<sub>2</sub>O – 0.03, Al<sub>2</sub>O<sub>3</sub> – ND.

### 2.2. Experimental setup

The conditions of exposing the ilmenite samples to the effect of high-voltage nanosecond electromagnetic pulse (HPEMP) and irradiation from the dielectric barrier discharge (DBD) in air under standard conditions were described in [16, 17]. The duration of sample treatment varied in the range  $t_{\text{treat}} = 10\text{--}150$  s. With the HPEMP effect, the duration of pulses was 4–10 ns. Pulse amplitude  $U \sim 25\text{--}30$  kV; strength of the electric field in the 3–5 mm interelectrode gap,  $E \sim 10^7$  V×m<sup>-1</sup>; rate of nanosecond pulse repetition  $f = 100$  Hz. In case of the barrier discharge generator (DBD), the electrode voltage in the barrier discharge cell was 20 kV; the length of the leading edge of a pulse, ~300 ns; the length of pulse, ~8 μs, and effective frequency of pulse repetition was ~15 kHz.

### 2.3 Research technique

Infrared spectra (FTIR) of ilmenite were recorded throughout the region of 4000–400 cm<sup>-1</sup> (spectral resolution, 4–6 cm<sup>-1</sup>) using a Nicolet-380 spectrometer equipped with a special Smart Diffuse Reflectance accessory. The morphology and defects of the ilmenite surface were studied via analytical electron microscopy on a scanning electron microscope LEO 1420VP equipped with an Oxford Inca 350 Energy Dispersive X-Ray EDX Microanalysis System.

The mineral's microhardness was determined according to Vickers method ( $HV$ , MPa) using the a PMT-3M microhardness tester and the standard operating procedure, adapted to geomaterials testing and described in [16]. The load on the indenter was 100 g, and the period of loading was 10–15 s. The electrokinetic (streaming, flow) potential (mV) of mineral particles (size  $\leq 50$  μm) was determined using a Microtrac ZETA-Check Zeta Potential Analyzer. The contact angle of wetting ( $\Theta^\circ$ ) of polished sections of the surfaces before and after energy treatment was measured with sessile drops of distilled water (“resting” on the surface) ~2–3 mm in diameter, following the

procedure in [17]. Analysis was done using a digital optical microscope and the ImageJ program with special DropSnake and LB-ADSA plug-ins [18].

### 3. Result and discussion

#### 3.1. Mechanism of the structural state modification of ilmenite surfaces under the effect of high-power electromagnetic pulses and dielectric barrier discharge

Ilmenite (titano-ferrite  $\text{FeTiO}_3$ , 42–62%  $\text{TiO}_2$ ; a mineral of variable composition) is one of the most common minerals in the Earth's crust and is a composite (double) oxide of the  $ABX$  type, where  $A$  is  $\text{Fe}^{2+}$ ,  $\text{Mg}^{2+}$ , or  $\text{Mn}^{2+}$ , and  $B$  is  $\text{Ti}^{4+}$  [4, 19]. The crystalline structure of ilmenite ( $ABO_3$ ) is based on a closely packed hexagonal oxygen lattice with metal atoms occupying two thirds of the existing octahedral positions, while the remaining third is vacant [19]. Ilmenite contains two different octahedral layers:  $A$  with  $\text{Fe}^{2+}$  cations and  $B$  with  $\text{Ti}^{4+}$  cations arranged entirely along the  $c$ -axis. Each  $\text{FeO}_6$  and  $\text{TiO}_6$  octahedron is connected by three edges with octahedra inside a layer, by a face with an octahedron of second-type atoms from a neighboring layer, and by the opposite face with a vacant octahedral position. Ilmenite has semiconducting properties (width of the bandgap,  $E_g = 2.5\text{--}2.9$  eV [4, 20]). Pure  $\text{FeTiO}_3$  is characterized by high resistivity [20]. The conductivity of natural ilmenite varies from  $10^{-5}$  to  $10^{-4}$  ( $\Omega \times \text{cm}$ ) $^{-1}$  [20]; the magnetic susceptibility is 68 to 960  $\text{emu} \times \text{g}^{-1}$ , its density is 4.6–5.2  $\text{g} \times \text{cm}^{-3}$ , and its Mohs hardness is 5–6 [4].

The infrared Fourier spectrum of ilmenite in its initial state (before electromagnetic effects) contained the following characteristic absorption bands caused by vibrations of structural groups in the crystalline lattice of the mineral [4]: the band in the spectrum with a maximum at  $490$   $\text{cm}^{-1}$  corresponds to valence vibrations ( $\nu$ ) of  $\text{Ti-O-Ti}$  bonds; the band at  $583$   $\text{cm}^{-1}$ , to valence vibrations of  $\text{Ti-O}$  bonds in  $\text{TiO}_6$  octahedra; the band at  $648$   $\text{cm}^{-1}$ , to valence vibrations of  $\text{Fe-O}$  bonds; the band at  $712$   $\text{cm}^{-1}$ , to valence vibrations of  $\text{Ti-O}$  bonds; and the band at  $1098$   $\text{cm}^{-1}$ , to deformation vibrations ( $\delta$ ) of  $\text{Fe-OH}$  bonds. The ilmenite spectrum also contained weak absorption maxima at around  $3135$  and  $1686$   $\text{cm}^{-1}$ , related to valence and bending vibrations of  $\text{OH}$  in the structure of the adsorbed water.

As a result of the nonthermal effect of high-voltage nanosecond pulses (HPEMP), the FTIR spectra of ilmenite contained additional lines at  $917\text{--}968$   $\text{cm}^{-1}$ , related to vibrations of  $\text{-O-O-}$ peroxy groups. The intensity of absorption lines varied at  $648$  and  $1098$   $\text{cm}^{-1}$ , and grew at  $580$   $\text{cm}^{-1}$  (the region of vibrations by  $\text{Ti-O}$  bonds in  $\text{TiO}_6$ -octahedra). Analysis of the dependence of the relative intensity of ilmenite spectral lines on the duration of electromagnetic pulse treatment ( $t_{\text{treat}} = 10\text{--}150$  s) showed that the content of  $\text{Fe-OH}$  groups fell (i.e., the surface of the mineral *dehydroxilated*) when  $t_{\text{treat}}$  was raised to 50 s. When  $t_{\text{treat}} \geq 50$  s, the surface *hydroxylated*. A similar tendency was also observed for the change in the content of  $\text{OH}$ -groups in the water molecules absorbed on the ilmenite surfaces. It should be noted that the relative intensity of the line at  $\sim 650$   $\text{cm}^{-1}$  corresponding to vibrations of  $\text{Fe-O}$  bonds also reached its maximum when  $t_{\text{treat}} = 30$  s.

One possible mechanism of the modification of the structural state and structure sensitive properties of ilmenite surfaces under the effect of high-voltage nanosecond electromagnetic pulses, is the transformation (destruction) of the mineral's crystalline structure, which consists of layers of two types of octahedra:  $\text{Fe}^{2+}\text{O}_6$  and  $\text{Ti}^{4+}\text{O}_6$ , alternating along the  $c$ -axis. Apparently, under the repetitive pulsed effect of a high-voltage electric field stronger than that of the mineral's grains dielectric strength ( $\geq 10^7$   $\text{V} \times \text{m}^{-1}$ ),  $\text{Fe-O}$  bonds break in the first type of octahedra, while  $\text{Ti-O}$  bonds in the second type do not undergo any destructive changes. Another possible mechanism of the changes in the FTIR spectra of ilmenite is the electrical disintegration and removal of fine films of iron oxides (hydroxides) from the ilmenite surfaces when  $t_{\text{treat}} \leq 30\text{--}50$  s, and the subsequent hydroxylation and/or oxidation of ( $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  iron ions) on the surfaces when  $t_{\text{treat}} \geq 30\text{--}50$  s, due to the effect of the products of spark microdischarge plasmas.

Dielectric barrier discharges (DBD) caused the following changes in the infrared spectra of ilmenite: there was an increase in the relative intensities of the lines corresponding to vibrations of Ti–O bonds in  $\text{TiO}_6$ -octahedra. The relative intensities of the lines of –O–O– peroxy groups grew as well, due likely to the oxidation of the mineral surfaces under the action of products (e.g.,  $\text{O}_3$ ,  $\text{H}_2\text{O}_2$ , NO,  $\text{N}_2\text{O}$  [15, 21]) of DBD low-temperature plasma (LPT). As the duration of treatment ( $t_{\text{treat}}$ ) grew, so did the intensity of the lines associated with water molecules adsorbed on the mineral surfaces. The dependence of the relative intensity of the Fe–OH lines on the duration of the DBD effect is generally nonlinear. The minimum concentrations of  $\text{O}^{2-}$ ,  $\text{OH}^-$  anions, and adsorbed  $\text{H}_2\text{O}$  on the ilmenite surfaces were reached at  $t_{\text{treat}} = 30$  s.

### 3.2. Effect of nanosecond electromagnetic pulses and dielectric barrier discharge on morphology, defects and structure sensitive properties of ilmenite surface

Extended fragmented traces of streamer discharges with a complex discrete internal structure and microcracks formed on the surfaces of polished ilmenite samples as a result of brief ( $t_{\text{treat}} = 10\text{--}30$  s) electrical pulse treatments (Fig. 1a). As the duration of the electrical pulse treatment grew to  $t_{\text{treat}} = 50$  s, paths of electric breakdown and crystallographically oriented microcracks formed that led to destruction of local regions of the mineral surfaces (Fig. 1b).

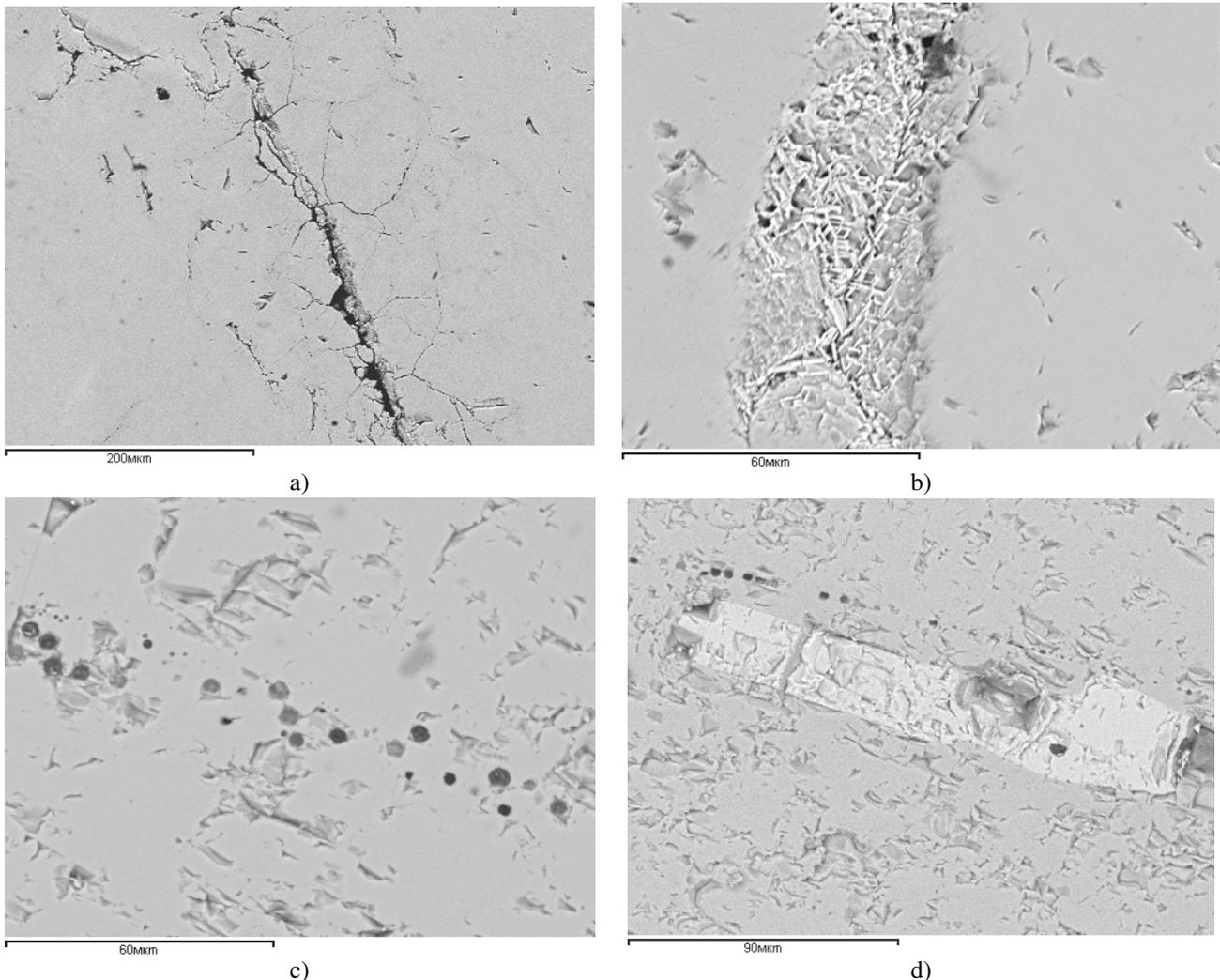


Fig. 1. SEM-images of ilmenite surface as a result of (a), (b) HPEMP and (c), (d) DBD treatment within 50 seconds ( $t_{\text{treat}} = 50$  s). Scales (a) 200  $\mu\text{m}$ ; (b), (c) 60  $\mu\text{m}$ ; (d) 90  $\mu\text{m}$ .

When the duration of nanosecond HPEMP treatment was extended, the softening of the ilmenite surface occurred and the mineral microhardness fell monotonically from ~670 MPa in the initial state to ~520 MPa ( $t_{treat} = 150$  s). The relative drop in microhardness  $\Delta HV_{max}$  was ~22.4%.

We established the *nonlinear (nonmonotonic)* character of the change in the electrokinetic potential and contact angle of surface wetting of ilmenite upon an increase in HPEMP treatment ( $t_{treat} = 10$ –150 s). As a result of brief ( $t_{treat} = 10$  s) electromagnetic pulse treatment of our mineral samples, the electrokinetic potential of ilmenite rose in the region of negative values (from -70 mV in the initial state to -74 mV). As the duration of treatment grew ( $t_{treat} = 50$ –150 s), the electrokinetic potential fell to the initial negative values of -70 to -69 mV. During the brief electrical pulse treatment of plane-parallel polished samples ( $t_{treat} = 10$ –30 s), the contact angle of mineral surface wetting ( $\Theta$ ) rose from 103.5° to 106.2°, due to the drop in the concentration of hydroxide compounds of iron, testifying to the stronger hydrophobic properties of the mineral surfaces. The value of  $\Theta$  fell continuously from 90° to ~72° when  $t_{treat} = 50$ –150 s, due to an increase in the concentration of OH-groups.

As a result of the DBD effect ( $t_{treat} = 10$ –150 s), the electrokinetic potential of ilmenite varied nonlinearly (nonmonotonically), depending on the duration of the barrier discharge irradiation. As a result of the low temperature plasma treatment of mineral particles at  $t_{treat} = 10$  s, the electrokinetic potential increased in the region of negative values, from -69.5 mV in the initial state to -76 mV. At  $t_{treat} = 30$ –150 s, the electrokinetic potential fell continuously to -16.5 mV. Increasing the duration of LTP treatment of mineral particles to  $t_{treat} = 300$  s caused the electrokinetic potential of ilmenite to rise to the initial negative values of -68 mV. The change in the microstructure and morphology of the ilmenite surfaces due to the DBD effect ( $t_{treat} = 10$ –150 s), caused a monotonic drop in the contact angle of surface wetting and microhardness of ilmenite: contact angle ( $\Theta$ ) decreased from 103.5° in the initial state to ~70° ( $t_{treat} = 150$  s), and microhardness ( $HV$ ) fell from 670 to 590 MPa at  $t_{treat} = 150$  s;  $\Delta HV_{max}$  was ~12%.

#### 4. Conclusion

On the example of a natural ilmenite, we demonstrated the possibility of increasing the efficiency of the structural and chemical modification of the mineral surface and directed changes in the mechanical, electrochemical, and physicochemical properties of complex oxide minerals by applying electromagnetic impulse effects. Using FTIR, we established, the following possible mechanisms of the nonthermal effect of HPEMP and DBD low temperature plasma irradiation, which modify the structural state of ilmenite surfaces: (i) the transformation (destruction) of the mineral's crystalline structure; (ii) the electrical disintegration and removal of fine films of iron oxides (hydroxides) from the ilmenite surfaces, and (iii) the subsequent hydroxylation and/or oxidation of  $Fe^{2+}$  to  $Fe^{3+}$  iron ions on the surfaces, due to the effect of the products of microdischarge plasmas.

The change in the microstructure and morphology of the ilmenite surfaces due to the HPEMP and DBD effects caused a softening of mineral surface and a monotonic reduction in the microhardness by 12–22% overall. Also, we established the nonlinear (nonmonotonic) character of the change in the electrokinetic potential and contact angle of surface wetting (in case of HPEMP) of ilmenite upon an increase in electromagnetic pulsed treatment ( $t_{treat} = 10$ –150 s). Our results testify to practicability and potential of using comparatively brief ( $t_{treat} = 10$ –30 s) electromagnetic pulse effects (HPEMP, DBD) in air under standard conditions on the titanium minerals for the structural chemical modification of surfaces, microhardness and physicochemical properties of natural ilmenite in order to improve efficiency of complex titanium ores processing.

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## 5. References

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