SYNTHESIS, MORPHO-STRUCTURAL CHARACTERIZATION AND ELECTROPHORETIC DEPOSITION OF AEGIRINE OBTAINED BY THE HYDROTHERMAL METHOD IN THE SI-FE-Na-H₂O SYSTEM

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Abstract. *Aegirine belongs to a group of minerals known as inosilicates. In this study, a fast and efficient procedure is proposed for the synthesis of aegirine nanoparticles by means of the hydrothermal process, starting from a suspension of simple hydroxide/silicate precursors. Structural properties of the obtained mineral were assessed by the XRD technique. It was found that aegirine was the only crystalline phase present. The expected needle-like morphology, characteristic of inosilicates, was confirmed by scanning electron microscopy (SEM). Through an appropriate selection of solvents and dispersants, an electrophoretic deposition and immobilization of aegirine on stainless steel was achieved. Native layers of aegirine displayed a very smooth morphology, while after calcination, a detachment of the layers from the stainless steel substrate and the appearance of cracks in the coating was observed. This phenomenon could be prevented by the use of appropriate additives.*

Key words: *aegirine, hydrothermal synthesis, structure, morphology, electrophoretic deposition*

1. INTRODUCTION

Aegirine is a member of the pyroxene group of inosilicates. The earliest reference to this mineral dates from 1835 in a note from Berzelius where the name aegirine was suggested in honor to Aegir the Scandinavian sea god (Berzelius, 1835), due to the fact that it was first described occurring in Rundemyr, Øvre Eiker, Buskerud, Norway. Before 1989, the name acmite (from Greek ἀκμή "point, edge") was accepted as synonymous of aegirine, in reference to the typical pointed crystals, but it is discredited nowadays (Morimoto, 1989). Aegirine commonly occurs in alkalic igneous rocks, carbonatites,

pegmatites, also in regionally metamorphosed schists, gneisses, iron formations, etc. It may occur as an authigenic mineral in shales and marls. Aegirine occurs as dark green monoclinic prismatic crystals. It has a glassy luster and perfect cleavage. The Mohs hardness varies from 5 to 6 and the specific gravity is 3.2 to 3.4.

The chemical formula of aegerine is $NaFeSi_2O_6$ in which the iron is present as Fe(III). In its composition, the sodium can be replaced by calcium or iron(II), while magnesium replaces the iron(III) to balance the charge. Moreover, aluminium can substitute the iron(III). In the structure of aegirine, iron is placed in single zig-zag chains of edge-sharing octahedral M1 sites, and sodium in the eight-fold coordinated M2 sites (Clark et al., 1989). The direct Fe-Fe distance within the chains is 0.319 nm whereas the separation of chains is 0.655nm in the ab plane, although the shortest Fe-Fe distance between chains is 0.618 nm (Clark et al., 1989). This type of structure has a Si-O-Fe bond type which resembles that of zeolites, where a proton can be anchored (ion exchange of the sodium that is compensating the negative charge).

Aegirine is used as a catalyst or an adsorbent for upgrading heavy oil and bitumen in order to convert this type of crude oil into more useful fractions like naphtha, kerosene, etc. There are studies which suggest possible abiogenic formation of hydrocarbons through the reduction of carbon dioxide in natural hydrothermal systems during water-rock interaction involving Fisher-Tropsch type reactions and the serpentinization of ultramafic rocks (Sherwood et al., 2013). Aegirine and Hedenbergite are responsible for the abiotic formation of hydrocarbons like methane, ethane and propane observed in natural crustal fluids like, for instance, in the East Pacific Rise hydrothermal vent (Sherwood et al., 2013). There is a study in which aegirine was used as a suitable catalyst for hydrocracking of methylcyclohexane and hydroxylation of phenol with hydrogen peroxide (Vitale, 2013). Aegirine can be deposited as a several microns thick film attached to the surface of a ferrous material, covering it completely to protect it from corrosion (Riman and Cho, 2001).

The preparation of synthetic aegirine materials is usually carried out at high temperatures or at high temperatures and pressures (Bennington and Brown, 1982; Redhammer et al., 2006; Nestola et al., 2006). In this short article, a template free hydrothermal method is reported to synthesize dendritic nano and microstructures of aegerine. The hydrothermal method is promising because it requires relatively low temperature (220°C) and gives crystalline powders without further heat treatment. In order to obtain nanorods it is important to make sure that nucleation occurs more readily than crystal growth. These results may contribute not only to defining structures and making morphologies more favorable but also to making a large-scale production of this mineral possible.

In this study, optimal conditions for electrophoretic deposition of aegirine onto a stainless steel substrate are presented and discussed. Immobilization of aegirine onto metalic substrates in the form of thin films could be important for its application as a catalyst and anti-corrosion coating, as well as for other specific purposes.

2. MATERIALS AND METHODS

2.1. Aegirine synthesis and characterization

Selected reagents, $Fe(NO_3)_3 \cdot 9\ H_2O$ and $Na_2SiO_3 \cdot 5\ H_2O$, were of analytical grade, purchased from Sigma-Aldrich and used as received. During synthesis, 4.24 g of $Na_2SiO_3 \cdot 5\ H_2O$ and 4.04 g of $Fe(NO_3)_3 \cdot 9\ H_2O$ were dissolved in 30 ml and 20 ml of deionized

water, respectively. Then, these two solutions were mixed by adding Na-metasilicate solution to iron(III) nitrate solution and stirred for 30 min on a magnetic stirrer. After that, the obtained brownish-yellow slurry was transferred into a stainless steel 316L autoclave. The closed reactor was heated in a furnace for 4 h at 220°C at the autogenous pressure of 19 bar, without stirring. At the end of the treatment, the autoclave was cooled to room temperature. The precipitate formed was filtered on Buchner funnel under vacuum and washed with plenty of deionized water. Finally, the samples were dried in air at 55 °C. The crystalline phases present in the obtained powders were assessed by X-ray diffraction (XRD), using a SiemensD500 diffractometer running with *CuKα* radiation. The microstructural characterization of the sample was completed by scanning electron microscopy (SEM) using a TESCAN VEGA TS 5130 MM.

2.2. Aegirine synthesis and characterization

The electrophoretic deposition (EPD) experiments were carried out at 20°C temperature, in a two-electrode system. The working electrode, which served as a substrate for the deposition of aegirine nanoparticles, and the counter electrode were placed in a Pyrex cell. Both electrodes were composed of 304 type stainless steel. Prior to any experiment the electrodes were mechanically polished and sonicated in deionized water and ethanol. After that they were electrochemically polished in a 0.1 M solution of oxalic acid with constant current of 0.5 A.

Isopropanol containing 1% of water was selected as a dispersion medium, and magnesium nitrate was used as a charging additive for the nanoparticles. The charging additive was first added to the solution, and then mixed for approximately 15 min to obtain a homogeneous charging medium. Subsequently, aegirine nanoparticles were slowly added to the solution containing the charging additive, and the suspension was then ultrasonicated for 30 min to create a uniformly dispersed system.

The two electrodes were immersed in the prepared EPD suspension and connected to a DC power supply (BK Instruments programmable DC power supply). The working and counter electrodes were then used as a cathode and an anode, respectively. Electrophoretic
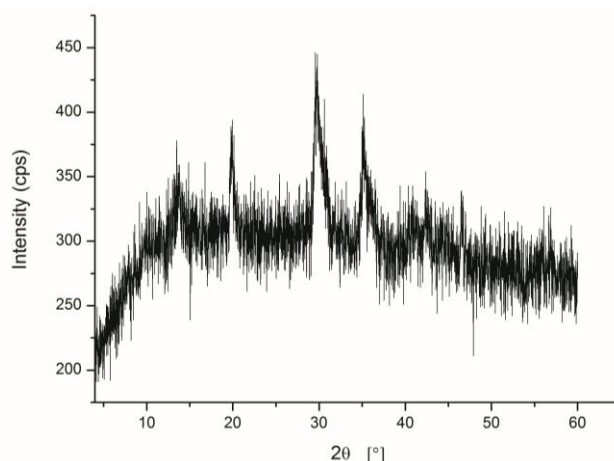
Fig. 1 The X-ray diffraction pattern of aegirine

deposition was performed at a constant voltage of 32 V for 3 min and a corresponding current of 0.01A, while the working distance between the cathode and the anode was 7 mm. The deposited specimens were dried at room temperature and then thermaly treated at two temperatures 450 and 650 °C. The microstructures of the native and calcined films on the stainless steel substrates were investigated using a stereo microscope Leica MZ16.

Table 1 Peak list

No.	2-θ(°)	Height(cps)	FWHM(°)
1	13.65	118	2.2
2	19.86	207	0.45
3	29.55	278	1.090
4	35.16	341.612	1.092
5	42.6	157.984	1.092
6	46.74	192.899	1.092

3. RESULTS AND DISCUSSION

To identify the crystal phases of the synthesized sample, powder X-ray diffraction (XRD) analysis was performed and the corresponding XRD pattern is shown in Figure 1. All the diffraction peaks are listed in Table 1 and could be clearly assigned to aegirine in accordance with the reported JCPDS data (card no. 18-1222).

No diffraction peaks arising from any impurity can be detected in the pattern confirming that the obtained product had only the crystal phase. The average crystallite size (D) of the particles was determined from the XRD line broadening measurement using the Scherrer's equation (1).

$$D = K\lambda/\beta_{hkl}\cos\theta \tag{1}$$

Here, K is a shape factor (0.9), λ is $Cu\ K_{\alpha1}$ radiation of 15.406 nm wavelength, β_{hkl} is the corrected full width at half maximum (FWHM) for instrumental broadening ($\beta_{hkl} = \beta_m - \beta_s$) in radians, whereas β_m is observed half-width and β_s is half-width of the standard sample, and finally θ is the scattering angle. The calculated crystallite size was 14 nm. In order to understand the strain associated with the sample due to lattice deformation, a line broadening analysis and calculations were carried out using the Williamson-Hall (W-H) method. Williamson and Hall proposed a good method for the separation of strain and size effects on broadening by looking at the peak width as a function of the diffracting angle (Christy et al., 2013; Yogamalar et al., 2009), according to Equation (2):

$$\varepsilon = \beta_{hkl}/4\tan\theta \tag{2}$$

Equations (3) takes into account both the Scherrer equation (1) and the volume-weighted average strain:

$$\beta_{hkl}\cos\theta = K\lambda/D + 4\varepsilon\sin\theta \tag{3}$$

where ε is the micro-strain. The strain value was obtained from the graph plotted from W-H method which is shown in the Figure 2.
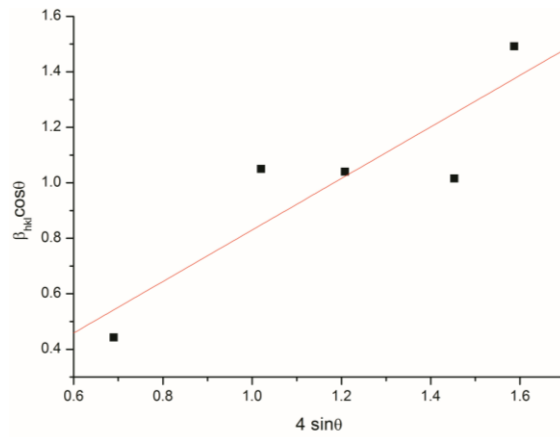
Fig. 2 The W–H analysis of aegirine (the strain ε is extracted from the slope).

A plot between 4 $sin\theta$ along the *x*-axis and $\beta_{hkl}cos\theta$ along the *y*-axis, gives the slope of the curve to determine the strain (ε) associated with the lattice dislocations. It was found that strain arising from lattice dislocation as calculated from Equation (3) is 0.929. W-H analysis revealed a very high value of microstrain in nanocrystals of aegirine indicating a lot of crystal imperfections, dislocations and distortions which significantly influenced peak broadening. For example, Siddiqui et al. (2014) reported recently that microstrain of synthesized CuO tetrapodes is 0.00217, which was negligibly attributed to peak broadening.
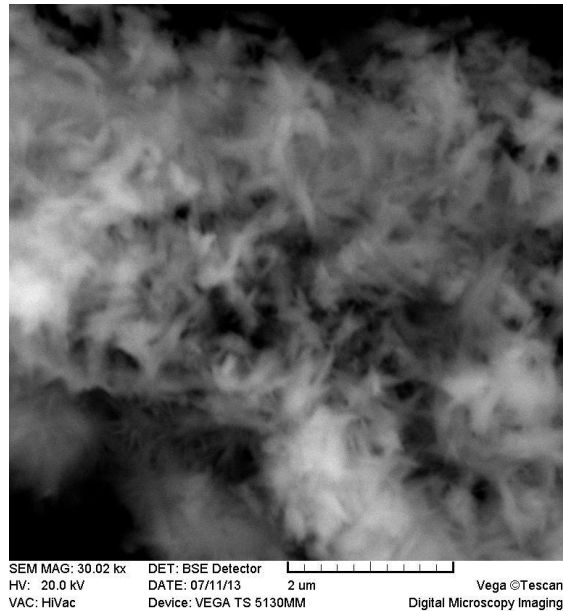

Fig. 3 SEM Micrograph of aegirine

Natural aegirine materials have a tendency to be produced as elongated crystals, much bigger (sizes in the mm or even cm ranges) than those produced under the hydrothermal conditions herein employed. The SEM micrograph in Figure 3 shows that the synthesized aegirine mainly consists of tiny needle-like crystals joined together forming dendritic aggregates.

There are a lot of techniques for the application of coatings onto metallic substrates such as physical vapor deposition, chemical vapor deposition, electrochemical vapor deposition methods, plasma technologies, spraying techniques, dip-coating, screen-printing or slip-casting etc. Among them, electrophoretic deposition (EPD) stands out as a particularly attractive technique because of its advantages of short formation time, simple apparatus, little restriction to the shape of the substrate, and no requirement for binder burnout as the green coating contains few or no organics. Compared to other advanced techniques, the EPD process can be made on a flat, cylindrical or any other shaped substrate with only minor change in the electrode design and positioning.

Electrophoretic deposition of aegirine onto a stainless steel substrate was achieved by the electrophoretic motion of a charged particle in an isopropanol-water medium under an applied electric field. In the present work, the isopropanol - water mixture was selected for the EPD suspension because only water-based EPD could cause oxidation processes onto the metallic anode, contamination of deposition layer and gas evolution (Mageshwari and Sathyamoorthy, 2013; Ferrari and Moreno, 1997; Ferrari and Moreno, 2000; Moreno and Ferrari, 2000). For these reasons the obtained coating is not uniform, has a lot of defects and consequently, intrinsic properties of the layer could be deteriorated.
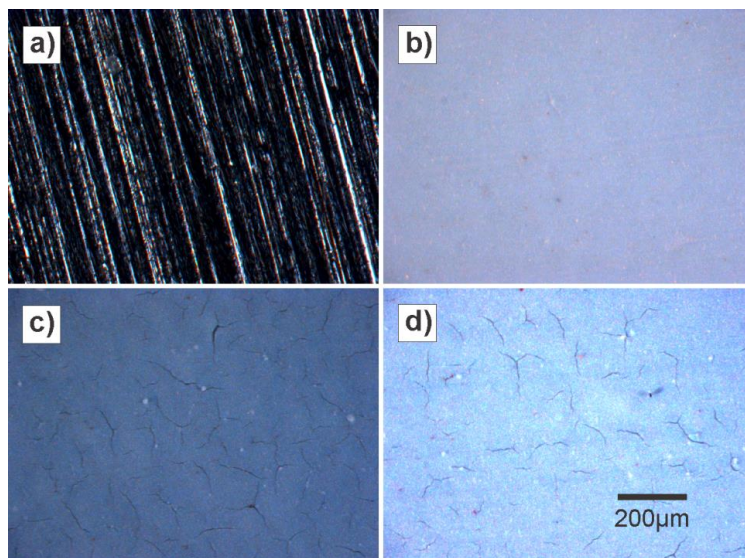
Fig. 4 Surface morphology at magnification of 115x: stainless steel substrate (a), native aegirine layer obtained by EPD (b), calcined aegirine layer at 450 °C (c) and calcined aegirine layer at 650 °C (d).

Based on a series of experiments, the EPD in this study was conducted at a constant voltage of 32 V for 3 min as an optimal condition. In the EPD process, the charged particle accumulates on the surface of the substrates, removing the solvent by electro endosmosis during the application of the electric field, inducing a flocculation of the particles (Fukeda et al., 2004; Bouyer and Foissy, 1999). The micrographs of the stainless steel substrate, native aegirine EPD layer and layers after calcination at 450 and 650°C, are shown in Figures 4a-4d. As can be seen from Figure 4b, the native aegirine layer was uniform and homogenous and no visible cracks were present on the surface. After calcination (Figures 4c and 4d) the deposited layers show discrete cracks of almost uniform length which is usual having in mind that during drying and sintering, the coating densifies and - as a result - shrinks, but the substrate typically does not change dimension significantly. During this process, the coating will develop tensile stress in it and these stresses will be relieved by the formation of cracks. By using certain additives, such adverse effects during calcination can be prevented, and tightly adhered aegirine layers can serve as an immobilized catalyst or corrosion protection coating. Consequently, it was clearly demonstrated that the EPD process is a simple and powerful method for creating a nano-structured, ceramic particle layer on steel. Moreover it was found that Mg^{2+} was an effective charging additive for the particles. The zeta-potential and conductivity of suspension was increased due to the presence of Mg(II), which was manifested as good electrophoretic mobility of particles accompanied with constant current of 0.01 A. There are a number of reactions in which a good catalytic activity aegirine was reported, and it is certain that further meticulous investigations of this mineral will open new areas of its application.

4. CONCLUSIONS

The proposed hydrothermal synthesis is a fast and easy way to obtain mineral aegirine. The resulting mineral has a needle-like structure, whose dimensions are in the nano range (14 nm), and their aggregation forms a coarse dendritic structure. It is very well-dispersed in a mixture of isopropanol-water (99:1) in the presence of Mg(II) in which it can be electrophoretically deposited on a conductive substrate such as stainless steel. The resulting coating was smooth and crack-free upon drying at room temperature. After calcination at 450 and 650 °C it leads to the appearance of cracks and coating loses its mechanical and adhesive properties.

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SINTEZA, MORFO-STRUKTURNA KARAKTERIZACIJA I ELEKTROFORETSKA DEPOZICIJA EGIRINA DOBIJENOG IZ Si-Fe-Na-H₂O SISTEMA HIDROTERMALNIM POSTUPKOM

Egirin je mineral inosilikatnog tipa. U ovom radu je opisan brz i efikasan hidrotermalni postupak za sintezu nanočestica egirina, polazeći od suspenzije jednostavnih hidroksida/silikata kao prekursora. Strukturne karakteristike dobijenog minerala su proučavane XRD metodom (rendgenska difrakcija praha), pri čemu je utvrđeno da se on sastoji isključivo od kristalne faze. Primenom SEM metode (skenirajuća elektronska mikroskopija), potvrđena je igličasta struktura minerala, karakteristična za inosilikate. Odabirom odgovarajućeg rastvarača i desperzanta, izvršena je elektroforetska depozicija i imobilizacija egirina na nerđajućem čeliku. Nativni slojevi egirina su posedovali glatku morfologiju, međutim, nakon kalcinacije uočeno je odvajanje prevlake od nosača od nerđajućeg čelika i pojava naprslina. Ovo se može sprečiti upotrebom odgovarajućih aditiva.

Ključne reči: *egirin, hidrotermalna sinteza, struktura, morfologija, elektroforetska depozicija*