Ti-doping of hematite by ion implantation method

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Abstract. Bulk α-Fe₂O₃ (hematite) sample with open porosity of 20 % and average pore size of 390 nm was obtained by spark plasma sintering (SPS). Ti-doping was carried out by ion bombardment method. Morphology, porosity, elemental and phase compositions were investigated. Rutile and titanomagnetite phases were formed after Ti-doping.

1. Introduction
Hematite is a very promising material in areas related to conversion of sunlight into chemical or electrical energy. α-Fe₂O₃-based materials are used for production of photocatalytic filters for water [1] and air [2] purification, photoanodes for water splitting, etc [3]. Efficiency of solar energy conversion is affected by structure and composition of the material that is used [4]. For example, gradient doping of hematite can be used to improve the conversion efficiency. Pengfei Liu et al. [5] showed that gradient Ti-doping doubles photocurrent values compared to homogeneous doping.

In this work, effect of titanium ion implantation on phase composition of hematite powders sintered by SPS method was investigated.

2. Synthesis and characterization of α-Fe₂O₃ powders
Initial powders were synthesized by ultrasonic spray-pyrolysis method. 10 % aqueous solution of Fe(NO₃)₃ was used as a precursor for atomization. Temperature of synthesis was set to 1000 °C. Morphology and elemental composition were investigated by scanning electron microscope (SEM) Vega Tescan 3 with EDX option. Phase composition was investigated by means of XRD technique on Difrey-401 under Cr radiation.

3. Consolidation of α-Fe₂O₃ powders and Ti-doping
Hematite powders were sintered by SPS method using Labox 650 Sinter Land system. Process parameters were: 200 °C/min heating rate, 750 °C temperature, 10 MPa pressure, 3 min duration. Graphite die was coated with boron nitride to prevent reaction between hematite and graphite. Porosity values were obtained according to GOST-18898-89 by hydrostatic density measurements (AD-1652).

Ti-ion bombardment was carried out with cathodic arc deposition installation in argon atmosphere. Titanium was used as a cathode. Evaporating arc current and bias potential between the cathode and the sample were 90 A and 0.9 kV, respectively. Duration of the bombardment was 15 min. Energy of the bombarding titanium ions was estimated by equation (1) [6] as ~1.8 keV. Magnetic separator was used to prevent a droplet phase from entering the substrate. The sample did not rotate during the ion implantation. The substrate was heated by plasma flow to 500 °C temperature, which was measured by pyrometer.

[1] and [2]...

The sample did not rotate during...
\[
W = W_o + Z \cdot \Delta U
\]

where \(W\) – bombarding energy; \(W_o\) – drift energy of ions; \(Z\) – average ion charge number; \(\Delta U\) – bias potential.

4. Results and discussion

Figure 1 shows SEM images of initial \(\alpha\)-Fe\(_2\)O\(_3\) powders before SPS treatment. It is seen that the produced powders were hollow spheres with average size \((d_h)\) of 971 nm. Average crystallite size calculated by means of Scherrer equation was 135 nm. Specific surface area of 6.29 g/m\(^2\) was obtained by BET method. This value corresponds to particles with 191 nm diameter. The results indicate that submicron spheres consist of smaller particles. SEM images of the \(\alpha\)-Fe\(_2\)O\(_3\) sample after SPS are shown on figure 2. It is seen that necks were formed between the particles, but the sample maintained its porosity. Average size \((d_p)\) of pores was 390 nm. Values of total and effective porosity were 37 and 20\%, respectively.

Figure 3 shows images of the surface (3a) and cross-section (3b) of the doped sample. As seen on the cross-selection image, thickness of the modified layer after Ti-ion bombarding was about 3.5 \(\mu\)m and the surface image shows that the sample is still porous. Measured values of total and open porosity of the sample after Ti-doping are close to the ones of the sample before doping and equal 35 and 17\%, respectively.

![Figure 1](image1.png)

**Figure 1.** Morphology and particle size distribution of \(\alpha\)-Fe\(_2\)O\(_3\) microspheres.

![Figure 2](image2.png)

**Figure 2.** Morphology and pore size distribution of consolidated \(\alpha\)-Fe\(_2\)O\(_3\) powders.

![Figure 3](image3.png)

**Figure 3.** Morphology of surface (a) and cross section (b) doped sample.

Surface composition of the sample after Ti-doping is presented in table 1.
**Table 1. Chemical composition after doping.**

| Element | Composition, % (at.) |
|---------|----------------------|
| Fe      | 7                    |
| O       | 64                   |
| Ti      | 29                   |

Figure 4a shows diffraction pattern for initial powder. It is seen that the pattern corresponds to \(\alpha\)-Fe\(_2\)O\(_3\) phase. Diffraction patterns of the sample after SPS and after Ti-doping are presented in figure 4(b). The sample after SPS has identical peaks as the precursor powder (\(\alpha\)-Fe\(_2\)O\(_3\) phase). After Ti-doping, the sample consisted of rutile (TiO\(_2\)), titanomagnetite (spinel) Fe\(_2\)TiO\(_4\) and hematite (\(\alpha\)-Fe\(_2\)O\(_3\)) phases.

Based on the assumption that the surface layers (figure 3(b)) subjected to the ion bombardment consist of titanium-containing phases (rutile and titanomagnetite), fractions of these phases can be estimated. Elemental composition data (table 1) was used for calculations. Estimated fractions of TiO\(_2\) and Fe\(_2\)TiO\(_4\) are 72 and 28 wt. %, respectively.

Titanomagnetite is formed as a result of reaction between anatase, magnetite (Fe\(_3\)O\(_4\)) and iron at temperatures above 300 °C [7]. Presumably, the flux of Ti ions leads to reduction of Fe\(_2\)O\(_3\) to Fe\(_3\)O\(_4\) and formation of anatase and iron. Reaction between these phases, induced by heating by the plasma flow, results in formation of titanomagnetite. Subsequently, the excess of anatase is converted into rutile.

**Figure 4.** X-ray diffraction patterns of the initial powder (a) and sintered sample before and after doping (b).

5. Conclusions

In this work we obtained \(\alpha\)-Fe\(_2\)O\(_3\) powders by means of ultrasonic spray-pyrolysis method. These powders were subjected to SPS treatment and subsequent Ti-ion bombardment. Phase analysis revealed that the surface of the sample consists of rutile, titanomagnetite and hematite. It was shown that ion bombardment technique does not significantly affect the values of total and open porosity of the samples (~2 % difference between the sample before and after Ti-doping).

Acknowledgments

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