The choice of iron-containing filling for composite radio-protective material

P V Matyukhin

Belgorod State Technical University after V G Shukhov, 46, Kostyukova St., Belgorod, 308012, Russia

E-mail: mpvbgtu@mail.ru

Abstract. The paper presents the data the composition of modern composite building materials including materials which in addition to high physical-mechanical have radio-protective properties. The article presents infrared researches and differential thermal data of fine-grained magnetite and hematite beneficiated iron-ore concentrates. The choice of the most suitable filling for new composite radio-protective building material engineering and development was made basing on the magnetite and hematite data presented in the paper.

1. Introduction

The development of the nuclear construction industry, as well as the widespread utilization of various nuclear power plants in different spheres of human activity, brings to the fore the biological protection issues in the facilities using such systems.

Various composite radio-protective building materials based on organic and inorganic components are successfully used in the construction and reconstruction of the facilities that are equipped with such nuclear power plants. Essentially the structure of the composite material is the base for various matrixes which have fillings with different proprieties depending on the function and application domain of the composite. These matrixes can have concrete, ceramic, polymer, metal base, while the fillings can be of organic and inorganic materials. The application domain of such materials is determined by their proprieties and exploiting conditions. The composition materials with metal matrix can be used not only as facing material, but as bearing constructions that can experience intense ionizing radiation and alternating temperatures. The following matrixes can be used for the development and production of modern composite radio-protective building materials: aluminum, lead, magnesium, nickel, uranium, tungsten, bismuth, thorium and metallic matrix based on different alloys [1-8].

One of the recent interesting and actual issues is the use of aluminum matrixes in the development of composite radio-protective materials. The usage of the pure aluminum as a metal matrix for composite material provides it with unique proprieties. Aluminum is a high-tech metal: it is perfectly processed by rolling, pressing, forming, forging; it resists flush blows (ductile). Aluminum pure has low resistance proprieties but it can form more durable alloys that have better physical-mechanical proprieties than aluminum pure and such alloys have also relatively small weight. Aluminum has high thermal conductivity and it can reflect heat flux. Those aluminum qualities show the actuality of its usage in the development of composite material and in the development of radio-protective material science.
Such materials as barite, limonite, metal scrap (in the form of cast-iron fractions), rebar scraps of strip and profiled metal, metal chips, highly dispersed iron-containing fillers etc. can be used as fillings for the composite materials on such base [9-15].

The most perspective fillings that can be used in the development and production of new composite radio-protective materials are magnetite and hematite iron-ore concentrates. The application of natural iron-ore raw material in the production of modern composite materials provide them not only with the additional durability, but with higher radio-protective properties. Such fillings are widespread in the nature (they are the part of existing ecosystems) that makes them more available and relatively cheap components for composite materials. Besides, the composite materials based on them will more likely meet environmental requirements. In my opinion, these fillings are more likely for the massive use in the development and production of new composite radio-protective materials, depending on the goals and objectives. This paper presents researches on the possibility of the application of magnetite and hematite iron-ore concentrate as a filling in the development of new composite radio-protective materials.

2. Materials and methods
Fine-grained magnetite and hematite beneficiated iron-ore concentrates of Kursk Magnetic Anomaly (KMA) were examined.

Iron-ore concentrate from Yakovlevsky deposit of KMA is high-grade hematite raw material with the following chemical composition (wt. %): Fe$_2$O$_3$ – 66.62; FeO - 28.15; SiO$_2$ - 4.41; Al$_2$O$_3$ - 0.17; CaO - 0.16; MgO - 0.29; K$_2$O - 0.09; Na$_2$O - 0.11. The density of the hematite concentrate is equal to 4770 kg/m$^3$; dark-grey color; Mohs scale of mineral hardness – 6-6.5. Hematite occur in granules of irregular shape. The crystallographic trigonal crystal system; conchoidal fracture, uneven.

Mineral composition is represented mainly by hematite (Fe$_2$O$_3$) with minor carbonate and siliceous impurities content (wt. %): hematite - 93.5; magnetite - 3.3; silicates - 0.5; quartz - 2.5; carbonates of 0.2.

Iron-ore concentrate from Lebedinskiy ore mining and processing enterprise is high-grade magnetite raw material with the following chemical composition (wt. %): Fe$_3$O$_4$ - 67.7; FeO - 27.1; SiO$_2$ - 4.25; Al$_2$O$_3$ - 0.26; CaO - 0.13; MgO - 0.36; K$_2$O - 0.09; Na$_2$O - 0.11. The density of the magnetite concentrate is equal to 4950 kg/m$^3$; black color; Mohs scale of mineral hardness – 6. Magnetite (Fe$_3$O$_4$) occur in needle-shaped granules, octahedral crystals, conchoidal fracture.

Concentrate mineral composition is represented mainly by magnetite with minor carbonate and siliceous impurities content (wt. %): magnetite - 94.3; hematite - 2.9; silicates - 0.3; quartz - 2.3; carbonates of 0.2.

In the result of 99.7-99.9% purification and chemical treatment of magnetite and hematite concentrates their mineral composition is represented by hematite (Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) with 15-150 µm fraction diameter. As a result, the following researches were held on the purified iron-ore concentrates.

The researches were performed with modern techniques and equipment:
- differential thermal analysis (DTA) curves were recorded using derivatograph (Firm «MOM», System Paulik-Erdey) with atmospheric heating rate 5 deg/min, weighed samples of 0.2-1.0 g;
- infrared spectra were studied using a two-beam spectrophotometer «Specord-751R», in the frequency range 4000-400 cm$^{-1}$. Samples for IR spectra were represented by transparent plates of potassium bromide, obtained by the samples compaction at the pressure of 1.5 MPa. Measurement frequency accuracy ± 2-5 cm$^{-1}$.

3. The IR-spectroscopy study of iron-oxide surface and their differential thermal analysis curves
IR spectroscopy methods detected the presence of hydroxyl groups on the surface of iron-oxides imparting the main property to the surface (Fig. 1, a). The infrared spectral analysis showed the presence of magnetite strip in the area 3490-3400 cm$^{-1}$, which according to the data [16, 17] belong to
the stretching vibrations of crystallization water (strip 3490 cm\(^{-1}\)) and OH-groups and adsorption water (strip 3400 cm\(^{-1}\)).

**Figure 1.** IR spectra of primary iron-oxides before (a) and after their thermal treatment at 180\(^\circ\)C (b): 1 - magnetite; 2 - hematite

According the data [16, 17] the absorption in the area 1050-1100 cm\(^{-1}\) corresponded to vibrations of water molecules coordination associated with surface. The presence of these stripes was traced both on magnetite and on hematite. The absorption stripes on the hematite were seen in the area 3420 cm\(^{-1}\) and 3360 cm\(^{-1}\) that corresponds to the stretching vibrations of OH-groups. The presence of the stripe 1640 cm\(^{-1}\) on the both iron-oxide forms was equal to HOH groups (adsorption water) deformation vibrations. Spectra curves in the areas 483 cm\(^{-1}\), 570 cm\(^{-1}\), 675 cm\(^{-1}\), 790 cm\(^{-1}\) on the magnetite were identified as Fe\(_3\)O\(_4\), the stripes 520 cm\(^{-1}\) and 620 cm\(^{-1}\), 800 cm\(^{-1}\) on the hematite are identified as Fe\(_2\)O\(_3\). The reason of existence of several iron stripes that appertained to free surface groups was that the oxide OH-groups can contact several metal atoms. The atoms of iron are the closest to OH-groups and their amount should influence certain influence on the vibration frequency of OH-groups.

The exploration of magnetite and hematite iron-ore concentrates were held to inoculate on their surface the metal to facilitate the interaction with the environment where they will have the role of fillings. The concentrates were thermally treated at the temperature of 180\(^\circ\)C (to establish constant mass) as at this temperature the physically planar water removes from the surface of iron-oxide that interfered in the modification process.

The data given let to suggest that the modification process of iron-ore concentrate particles to inoculate on their surface some certain material close in the structure to the composite matrix was highly possible. Such process would facilitate the interaction of the filling with the environment it will be put in. According that facts the IR-spectrometry researches of the concentrates that were thermally treated at the temperature of 180\(^\circ\)C (to establish constant mass) as at this temperature the physically planar water removes from the surface of iron-oxide that interfered in the modification process.

The magnetite and hematite IR spectra analysis showed (fig. 1, b) that the heating of primary products removed physically planar water. That fact was proved by the decreasing of intensive stretching vibrations of OH-groups after the increasing of temperature i.e. the removing of crystallized water (curve flattering in the area 3490-3400 cm\(^{-1}\) of magnetite and 3420-3360 cm\(^{-1}\) of hematite),
adsorption water (decreasing intensive 1640 cm⁻¹) and the removing of coordination associated with the surface water molecules (area smoothing 1050-1100 cm⁻¹).

Analyzing the data given we could do the following conclusion: there is a possibility to secure the modificatory on the iron-oxides. It is highly probably to do using hydroxide groups -OH on the surface. It is important to mention surface hydroxide groups that had the principal role but not the inner ones. Hydroxide groups participated actively in the reaction because the proton of hydroxide group is subacid and can enter in the exchange reaction.

There is not enough data to make any conclusion about the effectivity of iron-oxide systems as a filling basing on their possibility to react. Many composites can be received using high temperatures, that is why it is important to consider the condut of iron-oxide form at specified temperatures.

According the data [18, 19], magnetite (Fe₃O₄) and wustite (FeO) phases, that had about 67.7 and 27.1 wt.% of magnetite relatively in their compounds, when heating these phases transform into hematite (α-Fe₂O₃). The transformation of magnetite into hematite was processed via unordered phase – maghemite (γ-Fe₂O₃).

When heat magnetite had an exothermal effect in the interval 200-320°C that corresponded to a partial oxidization of magnetite to maghemite and an exothermal effect at the temperature 550-700°C that was characterized with the oxidization of the rest part of magnetite and the transformation of maghemite into hematite (Figure 2, a). While recording the thermograms there were found 2 small reversible endothermal effects of magnetic transformation at 553°C and 615°C when the first one was the transformation of Fe₃O₄ from ferromagnetic into paramagnetic condition, the second one was the α-Fe₂O₃ of ferromagnetic condition into paramagnetic [18, 19]. Wustite in its turn transformed into hematite in 320-390°C with the strong endothermal effect (fig. 2, b). Hematite (α-Fe₂O₃) showed no results in the thermal analysis (fig. 2, c).

![Figure 2. DTA iron-oxides curves: a) magnetite; b) wustite; c) hematite](image)

4. Conclusion

The fact that hematite showed no effect in differential thermal analysis let us consider this material as the most resistant of iron-oxide to any modification that gives it an advantage over magnetite and wustite. Any modifications are not desirable in the production of composite materials because such transformations are not advisable stage in the process of composite material production because the process of polymorphous modification (endo- and exo effects) can involve the changes of the whole system from the changes in microstructure of material to the material destruction on the cellular level with the appearance on microcracks. Therefore, the use of hematite iron-ore concentrate as a filling in
the development of new radio-protective building materials is more valuable task than the use of magnetite.

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