Influence of Synthesis pH on the Magnetic Properties of Copper Ferrite

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Introduction

Polycrystalline soft ferrites are magnetic materials that are stable, relatively inexpensive, easy to manufacture and are widely used in electronics, radio electronics, catalysis, medicine. Their successful use in these industries requires the presence of appropriate electrical and magnetic properties, which are primarily due to the structure [1]. Because spinel ferrites are an important class of ferromagnetic materials, they have been widely studied for many years. Many different methods of synthesis have appeared, such as microemulsion, coprecipitation, sol-gel, hydrothermal, sonochemical, which make it possible to obtain ferrites at low temperatures [2-4]. Moreover, the development of new methods for the synthesis of $CuFe_2O_4$ is of great importance due to its high electrical conductivity, high heat resistance and high catalytic activity. Copper ferrites have become important materials in recent years due to the possibility of their use as gas sensors, catalysts, in lithium-ion batteries, high-density recorders, ferrofluids.

The proposed plasma method has a number of advantages, such as short duration, product purity, simplicity, energy efficiency and dispersion of the final product.

It is known that $CuFe_2O_4$ exists in tetragonal and cubic structures. The tetragonal structure of copper ferrite has an inverted spinel structure with almost all Cu^{2+} ions in octahedral sublattices, and Fe^{3+} ions are divided between tetrahedral and octahedral sublattices. The cubic structure has a greater magnetic moment than the tetragonal one, because there are more copper ions Cu^{2+} in the tetrahedral positions compared to that in the case of the tetragonal structure.

Thus, the study of the influence of the conditions of synthesis of copper ferrite is necessary to understand the relationship between structure, heterogeneity and physical properties.

Experimental

$CuFe_2O_4$ nanoparticles were obtained by chemical precipitation from an aqueous solution of iron (II) sulfate and copper (II) sulfate, a method described in detail in [5].

The suspensions analyzed during the experiment were treated in a plasma discharge reactor for forty minutes. Changes in pH and potential were measured every two minutes. According to the obtained data for each group of solutions were plotted pH - treatment time and potential - treatment time, which are given below.

The first series of solutions was processed and analyzed at a constant ratio of copper to iron in both ferrite and the pH range = 7-12.

Samples of the second series were processed under conditions similar to the first series, but the difference was that every two minutes of activation of the solution, the pH value was again brought to its original value. For this purpose, a 0.4N alkali solution was used, which was added to the edges under constant stirring.

X-ray phase analysis of the samples was performed on a DRON-2 diffractometer. Operating mode of the X-ray source 40 kV, 30 mA. Scanning angles range 2θ: from 10 to 90° . Magnetic characteristics were determined using a vibrating magnetometer.

Results

Figures 1 and 2 show the dependences of pH and potential on the treatment time. There is a decrease in pH at the initial pH 7 and 8, at the initial pH 9-12 you can see its rapid drop to 20 minutes of activation (this corresponds to the middle of the activation time) and its further increase and establishment at a constant level. At the same time, the potential increases in a jump-like manner.

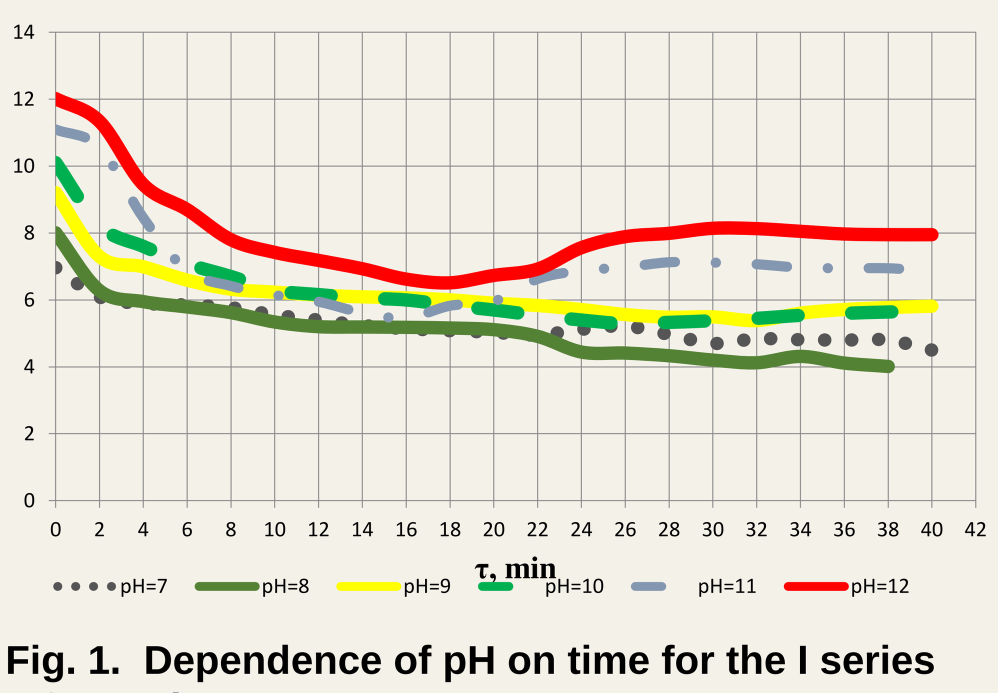

Fig. 1. Dependence of pH on time for the I series of samples

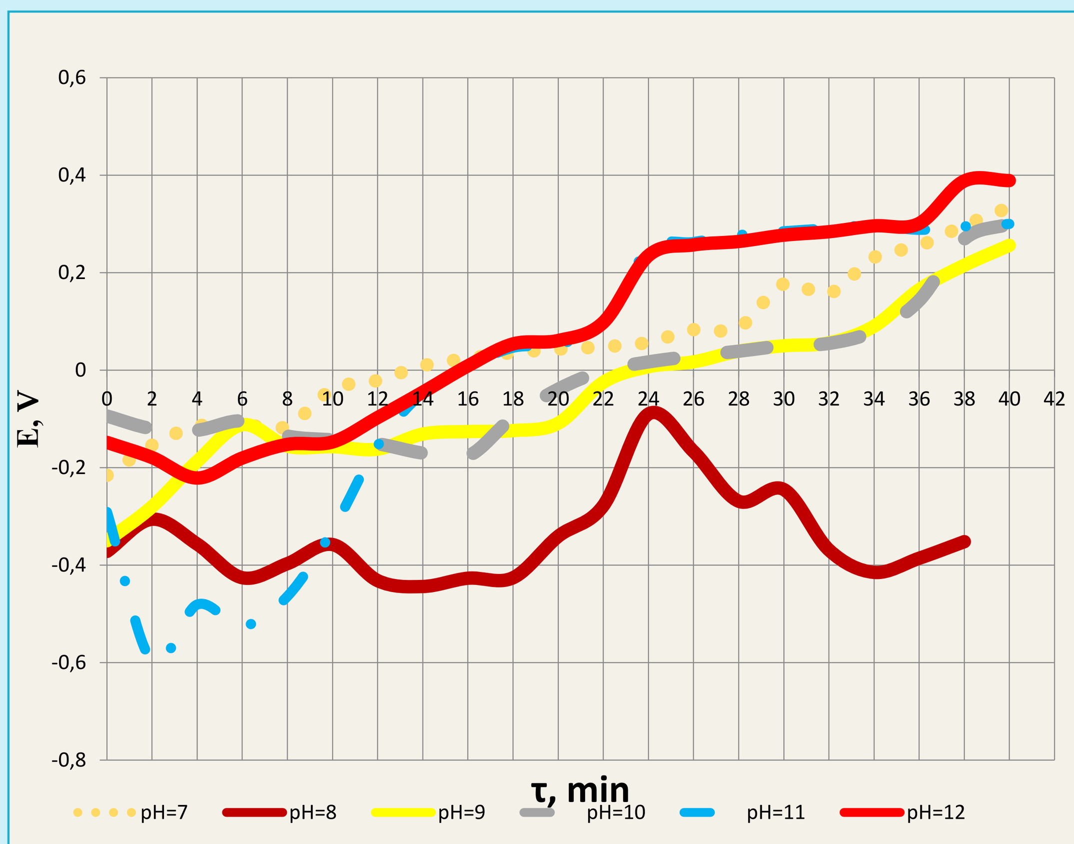

Fig. 2. Dependence of potential on time for the II series of samples

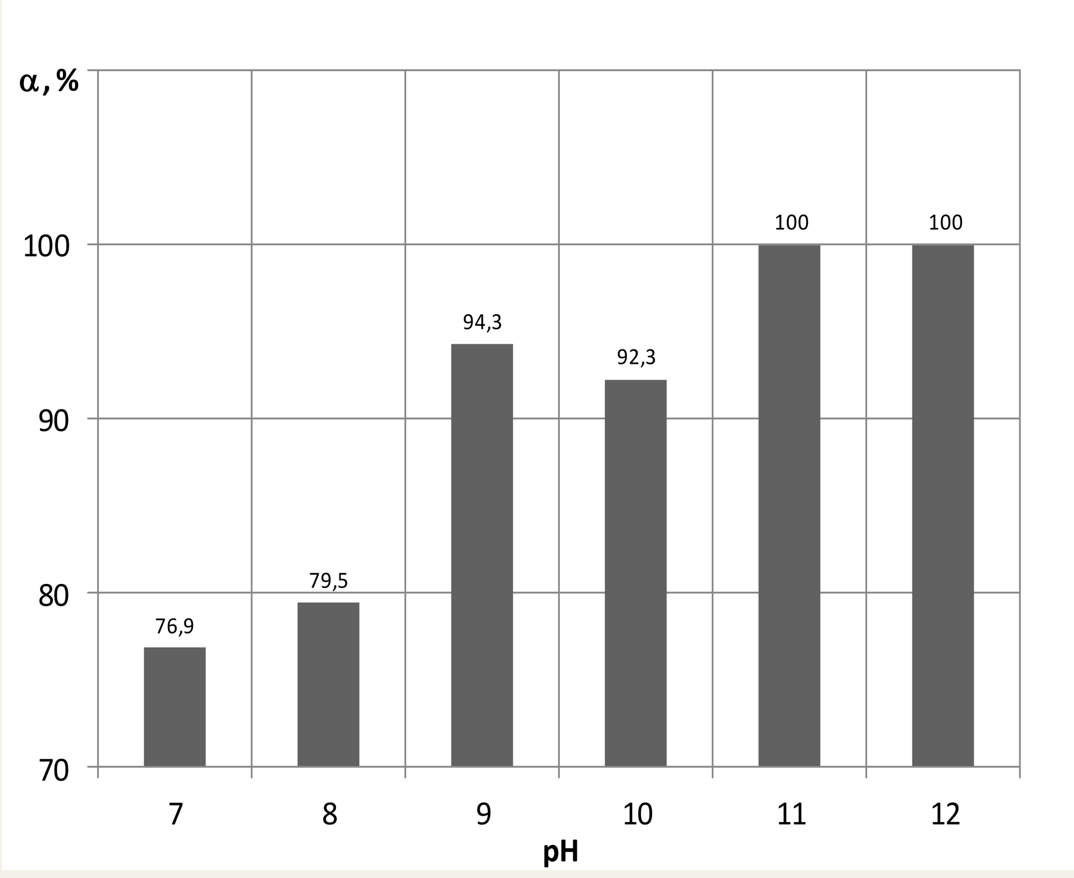

Fig. 3. Dependence of the degree ferritization on the pH value

The decrease in pH and increase in potential indicates the process of oxidation of iron (II) compounds to iron (III). An increase in the potential value may indicate the formation of various oxy-containing copper and iron compounds in the treated suspension, as these metals have several oxidation states. A constant pH value at the end of activation corresponds to the establishment of equilibrium(Fig. 3-4).

To analyze the degree of ferritization, the residual concentration of copper and iron cations, i.e. the concentration of cations in the filtrate, after treatment in a plasma chemical reactor at different pH values was determined.

That is, all three indicators change with jumps of different magnitudes. But in general, the following trend can be observed: at about 16-18 minutes the pH stops falling and begins to rise, the potential also increases with large jumps. The volume of alkali decreases rapidly, but also at some points there are jumps, which, accordingly, are caused by pH jumps.

It should be noted that the degree of conversion in this type of processing was 100% in all cases.

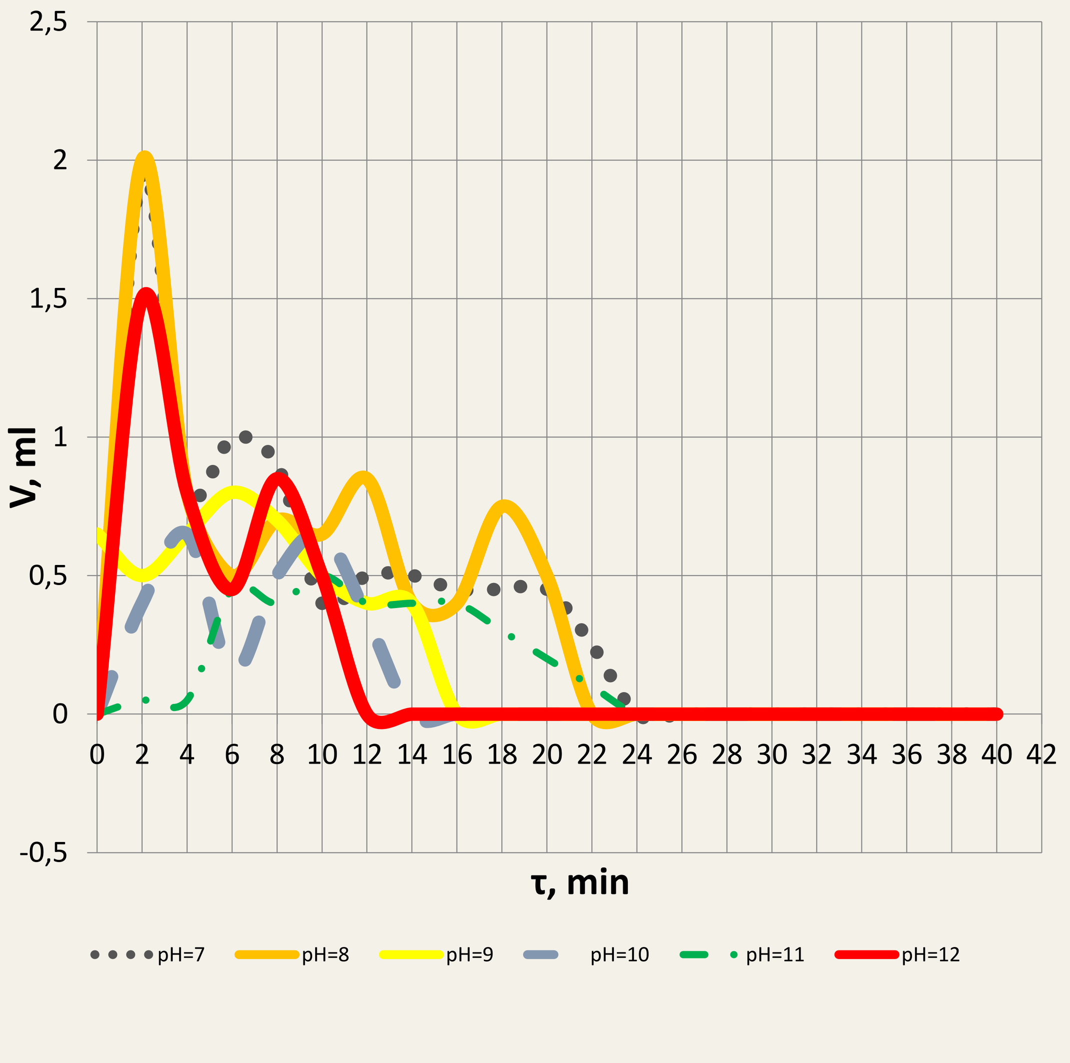

Fig. 4. The dependence of the volume of alkali on time for the second series of samples

Based on these graphs, it is possible to make assumptions about the possible mechanism of reactions that occur during the processing of samples in a plasma chemical reactor. Each of the peaks on the graph corresponds to the course of a certain process. We can assume that the process occurs in two stages, which are reflected in the form of two peaks in Figure 4.

The most important magnetic characteristics of the ferromagnetic material include the magnetization curve and the hysteresis loop. From these dependences it is possible to determine the main magnetic parameters of magnets, such as induction, magnetization, coercive force, magnetic permeability, magnetic anisotropy and others. The appearance of the magnetization curve and the hysteresis loop is determined by the magnetic structure of the material, namely the presence of domains, the interaction between them and their mobility, as well as the magnetic properties of individual atoms and molecules. The corresponding loops were processed, the generalized results of researches are given below in figure 5.

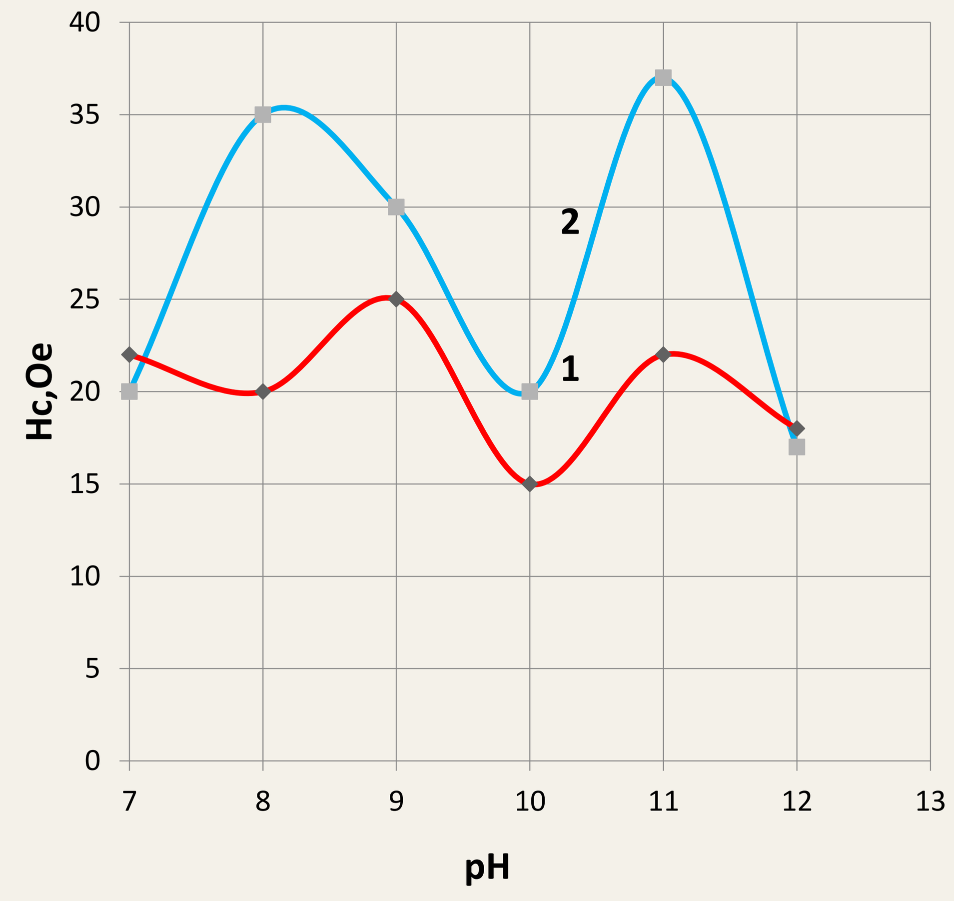

Fig. 5. Dependence of coercive force on pH for the first and second series of experiments

The value of coercive force is determined by the phase composition of the compounds that are formed. In the range of pH changes from 7 to 9, non-magnetic complex oxides and oxy-hydroxides of Fe-Cu are formed, this is due to the high speed of processes (Fig. 5). When the initial pH increases, the final product is copper ferrite, which has magnetic properties.

Increasing the pH to 12 leads to a decrease in magnetic properties due to the formation of a mixed oxide-ferritic phase also due to the acceleration of the oxidation process. That is, the dependence of the rate of oxidation reaction is extreme.

Conclusion

The use of new technologies for obtaining copper ferrites is very promising. The method of obtaining copper ferrite using non-equilibrium contact plasma can achieve a fairly high degree of conversion. Analyzing the results obtained, we can draw the following conclusions:

1. All the precipitates obtained have magnetic properties. The most magnetic is the sample with an initial pH = 11.

2. Optimal for providing copper ferrite with high magnetic characteristics is pH = 11.

3. With the gradual addition of alkali to the suspension, even at low initial pH, the residual concentrations of cations of iron and copper are almost zero, but the magnetic values are much lower than in the pH of the dynamic mode.

References

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