Studying the influence of supply pulse duration on the phase composition of iron oxides obtained by the plasma-dynamic method

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Abstract. Magnetic materials and in particular iron oxides are of a great practical interest. The magnetite phase and the unique epsilon phase of iron oxide can be especially pointed out. The main difficulty in the synthesis of the epsilon phase is connected with the fact that it can exist only in a nanoscale state and is extremely difficult to obtain. We used the method of direct plasma dynamic synthesis, which allows obtaining multiphase powders of iron oxides containing both the epsilon phase and magnetite. It was found that by varying the initial parameters of the power system, namely the pulse duration by increasing the capacitance of the capacitive energy storage, it is possible to influence the phase composition of the obtained products and to achieve the preferential output of the epsilon phase. In addition, in the mode with the maximum pulse duration, when the best product is obtained from the point of the epsilon phase output, the system efficiency of converting the stored energy into released energy significantly increases. In general, it has been established that such a regime is most favorable for the system operation for the purpose of the iron oxides synthesis.

1. Introduction

Magnetic materials are the most popular and used in various fields of science and technology. Among them iron oxides can be mentioned as the simplest compounds with high magnetic characteristics [1]. There are 7 non-hydrated phases of iron oxides with different structure and physical properties: α-Fe_2O_3 (hematite), β-Fe_2O_3, γ-Fe_2O_3 (maghemite), ε-Fe_2O_3, z-Fe_2O_3, FeO and Fe_3O_4 [2]. All of them have their own features, but the ε-Fe_2O_3 and Fe_3O_4 phases are of the greatest practical interest, due to their unique magnetic properties. For example, particles of epsilon phase have the highest value of coercive force among all known metal oxides (~23 kOe) and ferromagnetic resonance in the terrahertz range ~ 190 GHz [3–5]. Particles of the magnetite phase have a maximum saturation magnetization (92 G·cm^3/g) among ferrites at room temperature [1]. These properties can be useful for creating on their basis modern permanent magnets used for storing information and other electronics. Also, particles of the ε-Fe_2O_3 and Fe_3O_4 phases are non-toxic and highly resistant to corrosion. Despite a number of known method for magnetite synthesis, obtaining the epsilon phase is a rather difficult scientific task, due to the fact that it can exist only in a nanoscale state, as well as it is thermodynamically unstable [3, 6].

To date, many different methods have been developed that allow obtaining the magnetite phase (for example, solid-state reactions [7]; high-energy mechanosynthesis [8]; sol-gel method [9]; chemical coprecipitation [10]; microwave sintering; automatic combustion, conventional ceramic method, two-stage synthesis , etc.), however, the range of methods for obtaining the thermodynamically unstable ε-Fe_2O_3 phase is rather limited due to the fact that most synthesis methods also lead to the appearance

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of the hematite or maghemite phases. The most commonly used method is a sol-gel method, which is based on the following mechanism of phase transformations γ-Fe_2O_3 → ε-Fe_2O_3 → α-Fe_2O_3 when heated in the presence of a protective matrix. Despite its advantages and widespread occurrence, the sol-gel method also has a number of significant drawbacks, which mainly boil down to the need to use expensive precursors and complex chemical reactions, which leads to an increase in cycle time up to several days or even weeks [11].

It is known that the method of plasma dynamic synthesis has the following advantages: high reaction rate, low energy consumption, high achievable energy parameters in the synthesis process and high cooling rate, in a system based on a pulsed high-current coaxial magnetoplasma accelerator (CMPA). The possibility of using this method to obtain a multiphase product consisting of several modifications of iron oxide, including the rare epsilon phase and magnetite phase [12], has already been shown. In addition, in [13, 14], the possibility of controlling the phase composition by changing the process energy and oxygen concentration in the working chamber was shown.

In this regard, the aim of this work was to estimate the influence of the supply pulse duration on the phase composition of the iron oxides synthesized by plasma dynamic method. It was found that an increase in the pulse duration leads to obtaining the product with the predominant content of epsilon phase. More over, at longer pulse duration the overall efficiency of energy conversion in the system drastically rises up.

2. Experimental part

The studies were carried out in the known system based on a coaxial magnetoplasma accelerator (CMPA) used for generating and accelerating the plasma structure [13, 15]. The system of pulsed power supply from a capacitive energy storage device can be considered a sequential RLC-circuit. The capacitance (C) can be varied from 1.2 mF to 28.8 mF. The total inductance (L) of all in-series connected elements in the discharge circuit (inductance of capacitors, feeding coaxial cables, busbars), including the CMPA solenoid, does not exceed 2.0 μH. Active resistance (R) after beginning the arc stage does not exceed the order of 10-3 Ohms. With such values of the parameters, the following condition is satisfied:

$$R < 2\sqrt{L / \mathrm{C}} \tag{1}$$

This condition indicates the oscillatory-damped nature of the change in the discharge current in the short circuit mode. This is confirmed by experimentally obtained current oscillograms, one of which is shown in Figure 1.

However, the current attenuation coefficient, determined from real oscillograms, is significantly higher than the theoretical one, estimated by the expression:

$$b = R / 2L \tag{2}$$

This difference is due to a significant increase in the resistance of the arc discharge in the ignitron dischargers when the voltage polarity changes in an oscillatory mode. Under the conditions of the plasma-dynamic synthesis process in the full-wave mode, the increased resistance of the re-forming arc discharge in the accelerating channel of the CMPA will be included in the series circuit. This, naturally, will lead to a limitation of the current amplitude and a strong decrease in the efficiency of the process. Therefore, taking into account the actual operating conditions of the energy storage device with ignitron dischargers, the half-wave power supply mode of the CMPA is used. The duration of the current rise stage in these conditions up to a maximum, during which the CMPA consumes more than half of the supplied energy, and the maximum discharge power develops, can be estimated from the Thomson equation:

$$\frac{T}{4} = \frac{\pi}{2}\sqrt{LC} \tag{3}$$

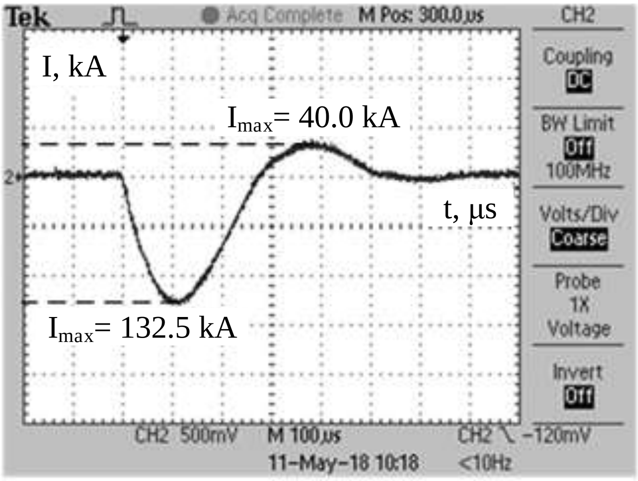

Figure 1. Short-circuit current oscillogram in the system at charging voltage of 500 V and capacitance of 28.8 mF.

From the formula 3 it becomes obvious that the most acceptable way to change the duration of a power supply pulse while maintaining high efficiency in the use of stored energy is to change the capacitance value of the capacitive energy storage that can be provided by its partitioned circuit. On this basis, experimental studies with the different supply pule duration were carried out at the following values of the capacitance: C_1 = 7.2 mF, C_2 = 14.4 mF, C_3 = 21.6 mF, C_4 = 28.8 mF. To save the value of stored energy W_c at the same level of 64-65 kJ in every experiment the charging voltage U_c was changed from 4.25 kV to 2.10 kV, respectively. The working chamber was filled with the technically pure oxygen at a pressure of 10^5 Pa.

3. Results and discussion

In order to study the influence of the supply pulse duration t_{pul} on the phase composition of the plasma dynamic synthesis products, a series of experiments were carried out with the varied capacitance value from 7.2 mF to 28.8 mF. The main data for a series of experiments are given in table 1. It should be noted that with an increase in the pulse duration t_{pul} both the efficiency of energy conversion and the mass of obtained powder m enhance almost twice. It indicates that system work with the enhanced capacitance positively affects the process productivity at the same initial parameters. Moreover, the decrease in the charging voltage U_c positively influence the lifetime of capacitor banks.

Table 1. Data of experimental series.

No.		1	2	3	4
Charging voltage, U_c	kV	4.25	3.00	2.45	2.10
Capacitance, C	mF	7.2	14.4	21.6	28.8
Charging energy, W_c	kJ	65.0	64.8	64.0	64.8
Released energy, W	kJ	30.0	43.0	49.5	58.0
Energy efficiency, W/W_c	%	46.1	66.3	77.3	89.5
Pulse duration, t_{pul}	µs	280	400	500	550
Powder mass, m	g	4.5	7.6	8.0	8.9

The obtained samples of powdered materials were investigated by the methods of X-ray structural and phase analysis. Typical XRD-pictures of the plasma dynamic synthesis products in comparison with the reference cards from the PDF4+ database are shown in Figure 2.

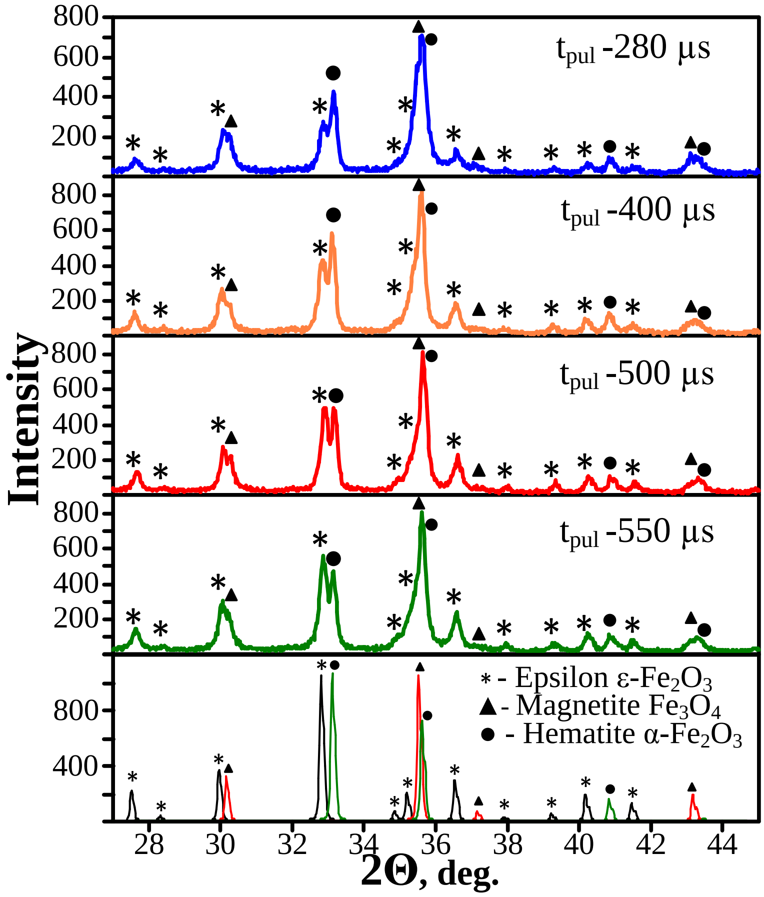

Figure 2. XRD-pictures of plasma dynamic synthesis products at various supply pulse durations t_{pul}.

An analysis of XRD pictures allowed us to establish that the powder synthesized with a minimum supply pulse duration $\boldsymbol{t_{pul}}$ = 280 µs is characterized by the presence of strong reflections corresponding to the phases Fe_3O_4 and ε-Fe_2O_3. An increase in $\boldsymbol{t_{pul}}$ leads to an increase in the relative intensities of the ε-Fe_2O_3 reflections at practically unchanged intensities of the reflections corresponded to the α-Fe_2O_3 phase. Thus, it may be concluded that a possible increase in the ε-Fe_2O_3 content occurs due to a decrease in the content of the Fe_3O_4 phase. This is unambiguously confirmed by a change in the numerical estimates of the percentage and the values of the main parameters of the crystalline phases, depending on their type (table 2).

The obtained results, given in table 2, make it possible to establish a pattern for increasing the yield of the ε-Fe_2O_3 phase with an increase in the pulse current flow duration in the power supply circuit. To determine the main factor affecting the increase in the output of epsilon phase with a change in the pulse duration, the oscillograms of the arc discharge currents, shown in Figure 3, were analyzed.

Table 2. Results of full-profile structural and phase analysis of synthesis products.

Phase	t_{pul}, µs	Mass content, wt. %	Lattice parameters, Å		CSR, nm	Δd/d ·10^{-3}
			Exp.	PDF4		
ε-Fe_2O_3	280	31.3	a: 5.10 b: 8.79 c: 9.46	a: 5.0950 b: 8.7900 c: 9.4400	36.0	1.0

	400	40.4	a: 5.09 b: 8.78 c: 9.47		43.5	0.6
	500	46.1	a: 5.08 b: 8.77 c: 9.46		48.0	0.2
	550	50.1	a: 5.08 b: 8.78 c: 9.46		56.0	1.2
Fe_3O_4	280	45.7	a: 8.37	a: 8.3700	29.5	1.9
	400	36.6	a: 8.36		31.0	1.7
	500	31.4	a: 8.33		36.0	2.4
	550	27.9	a: 8.35		40.0	2.3
α-Fe_2O_3	280	23.0	a: 5.03 c: 13.75	a: 5.0200 c:13.7350	124.5	1.3
	400	23.0	a: 5.03 c: 13.74		104.0	0.3
	500	22.5	a: 5.03 c: 13.71		122.5	1.6
	550	22.0	a: 5.03 c: 13.74		110.0	1.1

As noted in earlier works [13,14], the formation of the epsilon phase, apparently, should occur when a liquid-phase material is sputtered from the boundary of a shock wave, in the front of which high pressures and temperatures occur. The formation of a zone with high P,t-parameters occurs during the formation of the classical form of a shock-wave structure with a region of the Mach disk. When the iron-containing material passes through the boundaries of the Mach disk, it is subjected to high pressures and temperatures and starts reacting with oxygen. It was previously found that in the system under consideration the formation of a Mach disk occurs when the arc discharge current approaches its maximum. Thus, the time Δt_{max}, when the current is near its maximum value, can characterize the quasi-stationary state of the shock-wave structure of a supersonic flow [12]. With the existence of a quasi-stationary state, the most favorable conditions are created for the occurrence of a plasma dynamic reaction at the boundary of a shock wave with the formation of epsilon nanocrystallites.

Taking into account the system features described above, it was proposed to estimate the time Δt_{max} in each of the experiments performed. To do this, taking into account the known relationship between the formation time of a shock-wave structure stable form and the nature of the arc discharge current oscillogram [12], the conditional ten-percent zone is selected, marked with a dotted line in Figure 3, which is used to estimate the lifetime of the quasi-stationary expiration mode. As can be seen from Figure 3, with an increase in the pulse duration, the time Δt_{max} also increases. This indicates that the quasi-stationary state of the shock-wave structure is maintained for a longer time period, and the probability of the epsilon phase formation rises up. The objectivity of these judgments is confirmed by the results of full-profile X-ray phase analysis, indicating that the ε-Fe_2O_3 yield directly depends on the duration of the quasi-stationary supersonic plasma jet flow, which is determined by the duration of the pulsed power supply.

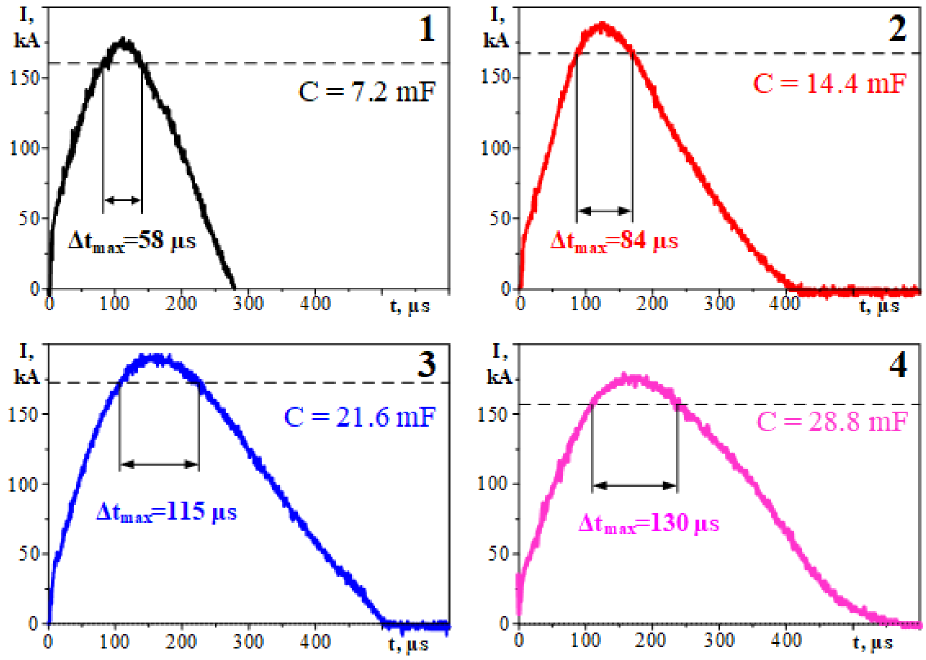

Figure 3. Oscillograms of arc discharge currents at different pulse durations.

4. Conclusion

Thus, evaluating the complex of the conducted studies to estimate the influence of supply pulse duration on the work of the system based on coaxial magnetoplasma accelerator the following conclusions can be made:

- The pulse duration in the considered system depends on the initial parameters of the RLC-circuit and can be changed by increasing the capacitance of the capacitive energy storage;
- The output of ε-Fe_2O_3 phase in the plasma dynamic synthesis products directly depends on the duration of the power supply pulse and the time when the system is at the maximum of its energy parameters;
- The efficiency of the energy conversion drastically rises up from 45% to ~90% in the case of system work with the higher pulse duration.

Acknowledgments

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