Optimizing the process of plasma dynamic synthesis for increasing the yield and purity of ε-Fe_2O_3 phase

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Abstract. Various crystalline modifications of iron oxide are widely used in different fields of science and technology, however, a special attention has recently been paid to the synthesis of the epsilon phase ε-Fe_2O_3. The existing problems connected with the synthesis and production of this phase in the form of a dispersed powdered product significantly limit the possibilities of its application and studying the properties. In this regard, the search and development of high-performance method for the synthesis of the ε-Fe_2O_3 phase is an urgent task. In this paper, the possibility of optimizing the well-known method of plasma dynamic synthesis for obtaining products with a high content of the ε-Fe_2O_3 phase was studied. The influence of the power supply pulse duration on the energy parameters of the synthesis process and the characteristics of the powdered products were studied in detail. It was established that an increase in the pulse duration due to the introduction of an additional inductance into the discharge circuit while simultaneously maintaining the magnitude of the arc discharge current at a level of 120 kA allows obtaining a product with the epsilon phase content of ~ 65 wt.%.

1. Introduction

In the last 25 years, much attention has been paid to the development of methods for synthesizing the magnetic materials and, in particular, the epsilon phase of iron oxide, due to a number of its unique features: 1) the greatest value of the coercive force at room temperature (~ 28 kOe) among all known simple metal oxides; 2) significant ferromagnetic resonance in the millimeter wavelength range; 3) magnetoelectric features that are not observed in other phases of simple metal oxides. Despite the fact that the first mention of this phase dates back to the 1930s [1], today there are about 150 publications in the world, the authors of which declare the implementation of ε-Fe_2O_3 synthesis mainly by the sol-gel method or a combination of the sol-gel method and the reverse micelle method (~ 85% of all published works) [2–5]. Using the sol-gel method, in addition to the well-known advantages, is characterized by large time costs, low product yield and the need for subsequent purification from the protective matrix of SiO_2 [6], designed to suppress crystal growth and phase transitions. It is known that the epsilon phase of iron oxide can exist only in a nanoscale state with crystallite sizes less than 100 nm and turns into hematite (α-Fe_2O_3) at temperatures of 700–800°C [7]. These features, as noted in the literature [8–11], are the main obstacles to the synthesis of other traditional methods. They do not also allow achieving a high yield of ε-Fe_2O_3 using most standard electrophysical methods based on

powerful high-voltage sources and stationary high-frequency, spark and arc discharges due to high temperatures in the reaction zone.

However, as it was shown earlier [1], by using some electric arc methods it is possible to obtain epsilon phase in a small amount. The plasma dynamic method based on a high-current high-voltage coaxial magnetoplasma accelerator (CMPA) of the erosion type can be attributed to these methods. The accelerator generates a pulsed supersonic electric-discharge plasma jet, in which the synthesis and formation of highly dispersed particles is observed [12–15]. A distinctive feature and advantage of the method is that it is realized at a voltage of 1–5 kV in a short time of about 10^{-3} s and does not require the use of high vacuum and pressure. The plasma flow rate of more than 3 km·s^{-1} provides a high sputtering and crystallization rates that makes it possible to obtain various metals and their compounds in the nano-dispersed state.

Using this type of system, it was previously shown that it is possible in principle to obtain the epsilon phase of iron oxide in a dispersed state as part of a heterophase product containing also magnetite and hematite [16]. However, under normal process conditions, the yield of the desired phase rarely exceeds 50 wt.%. In this regard, the research for ways to optimize the process from the standpoint of increasing both the product mass and the purity of the epsilon phase output is an important task.

This work shows the possibility to increase the ε-Fe_2O_3 content by increasing the duration of the power supply pulse of a coaxial magnetoplasma accelerator, both by increasing the capacitance of the energy storage device and by introducing additional inductance into the discharge circuit. It is noted that an increase in the time of quasi-stationary plasma jet flow leads to an increase in the epsilon phase content in the final product up to 65 wt.%.

2. Experimental

The CMPA-based system for implementing the plasma dynamic process typicall consists of three main elements: 1) capacitive energy storage; 2) coaxial magnetoplasma accelerator and working chamber. Typical design and function of CMPA-based system were considered earlier [17]. A special feature of the capacitive energy storage is its partitioned design (figure 1), which allows power supply of a CMPA with the ability to change the initial energy parameters (maximum operating voltage U_c = 5.0 kV, maximum capacitance C = 28.8 mF, maximum charged energy W_c = 360 kJ). The energy storage is based on pulsed capacitors IS5-200, recruited in a section with a capacity of 1.2 mF each, which are activated by supplying control signals from a multichannel delayed pulse generator (DPG) by means of power keys (PK) from the signal of the control blocks (CB). By varying the number of capacitor sections involved in the work, it is possible to adjust the parameters of the circuit and thereby influence the plasma dynamic synthesis process.

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 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} Ohm.

For the system under consideration, the Thompson equation $T = 2\pi(LC)^{1/2}$ is true, according to which the duration of the flowing process depends on the inductance and the capacitance of the circuit. From this equation 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, in order to study the influence of the pulse duration t_{pul}, experimental studies with the different supply pulse duration were carried out at the following values of the capacitance: C_1 = 7.2 mF and C_2 = 28.8 mF, which is the maximum value for the considered capacitive energy storage. To save the value of stored energy W_c at the same level of 64–65 kJ in these experiments the charging voltage U_c was changed from 4.25 kV to 2.10 kV, respectively. To obtain even longer pulse durations t_{pul} than 550 μs,

the second method was used with the inclusion of an additional powerful solenoid with an inductance L_{add} = 6.4 μH in the sequential RLC circuit, as shown in figure 1.

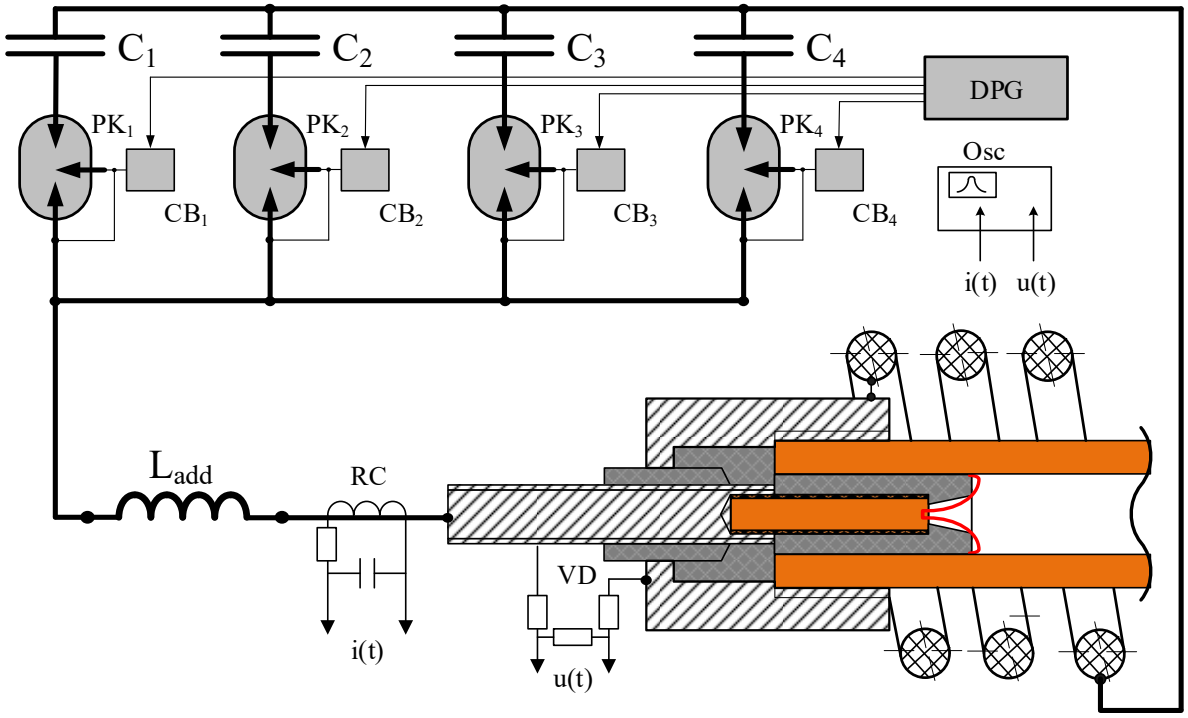

Figure 1. The sketch-map of the system for plasma dynamic synthesis of iron oxides with the additional inductance L_{add} in the discharge circuit.

The series of experiments was carried out in order to understand the influence of the pulse duration on energy characteristics of the process as well as the phase composition and the mass of synthesized iron oxide powders. In every experiment the working chamber, preliminary evacuated, was filled with oxygen (O_2) atmosphere at normal conditions.

Synthesized powders were investigated using X-Ray diffractometry (XRD) method. The XRD analysis was carried out using Shimadzu XRD7000S diffractometer with the counter monochromator Shimadzu CM-3121. The database PDF2+ and the software PowderCell 2.4 were used to provide respectively qualitative and quantitative analyses of XRD patterns. The energy characteristics were recorded at every experiment using Ohmic voltage divider (VD) and Rogowski coil (RC).

3. Results and discussions

The initial energy parameters of working cycles at different charging voltage U_c, capacitance C and additional inductance L_{add} are presented in table 1. Comparing experiments 1 and 2 it is possible to see that an increase in the capacitance of the energy storage device leads to a growth of the process duration t_{pul} that, respectively, affects the increase in the released energy W, efficiency of converting the accumulated energy into released W/W_c, electro-erosion from the walls of the acceleration channel m and the mass of the final powdered product m_{pow}. At this, there is a practical equality of the arc discharge current amplitudes I_m in each of the noted experiments (figure 2). A comparison of experiments 2 and 3 makes shows that despite the obvious increase in the process duration with the introduction of additional inductance L_{add} into the discharge circuit, at the same charging parameters U_c = 2.10 kV, C = 28.8 mF a significant decrease (almost 3 times) in the arc discharge current amplitude is observed. When there is a current flow with such relatively low parameters, it leads to a slight electro-erosion of the accelerator channel and it does not allow obtaining the product mass

necessary even for X-ray diffraction measurements. In this regard, experiments with the introduction of additional inductance were carried out with an increased amount of stored energy W_c due to an increase in the charging voltage U_c.

Table 1. Main energy parameters of the working cycles in the series of experiments.

No. exp	U_c (kV)	C (mF)	L_{add} (μH)	W_c (kJ)	W (kJ)	W/W_c (%)	t_{pul} (μs)	I_m (kA)	m (g)	m_{pow} (g)
1	4.25	7.2	–	65.0	30.0	46.1	280	180	4.5	3.46
2	2.10	28.8	–	64.8	58.0	89.5	550	170	8.9	7.66
3	2.10	28.8	6.4	64.8	18.0	27.8	1100	50	0.1	0.02
4	2.20	28.8	6.4	70.0	22.7	32.4	1130	78	0.5	0.20
5	2.80	28.8	6.4	113.0	61.8	54.7	1350	121	13.5	4.32

Such a change in the parameters logically led to an increase in the current amplitude up to 78 kA at $U_c = 2.20$ kV (exp. No 4) and 113.0 kA at $U_c = 2.80$ kV (exp. No 5) that is clearly seen in the corresponding waveforms (figure 2). At the same time, the pulse duration t_{pul} was increased almost 2.5 times in comparison with experiment number 2. At these conditions, the electro-erosion mass was increased by 50% with a significantly smaller amplitude of the power supply current. This can be considered as a positive thing, both in terms of improving the system performance, and reducing the electrodynamic loads on the main structural elements of the CMPA.

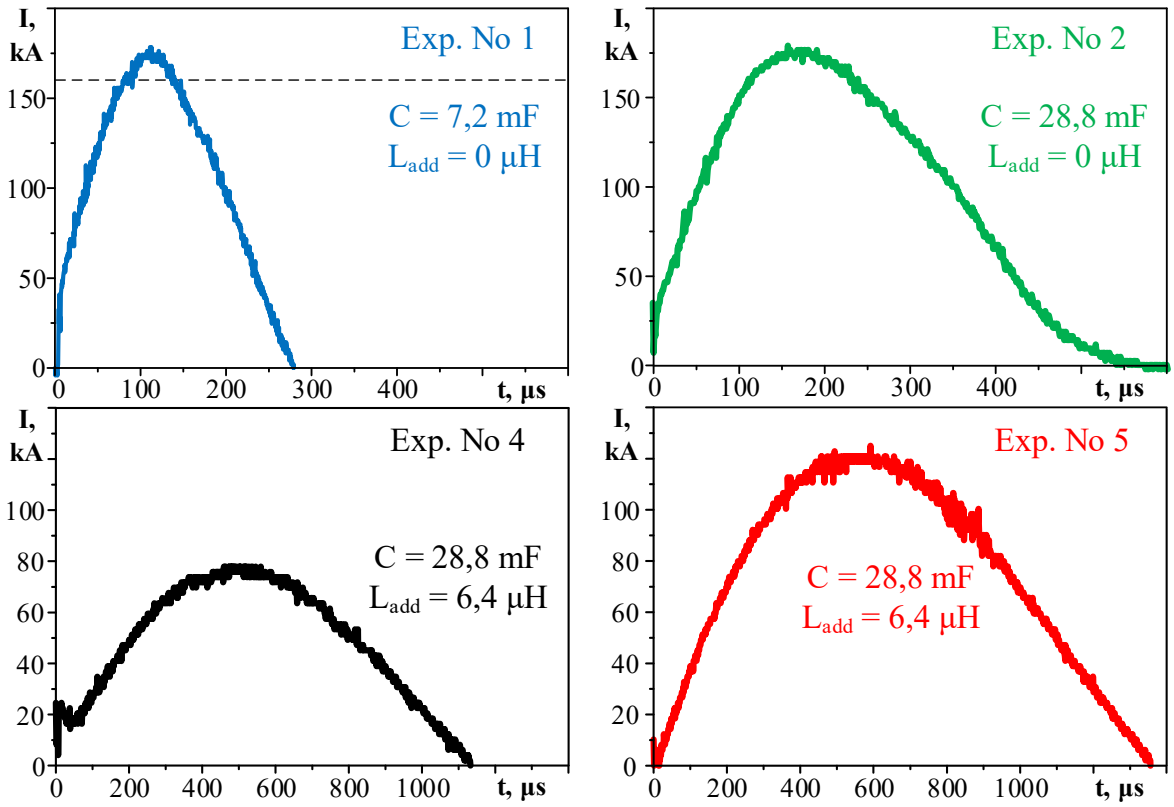

Figure 2. Current waveforms in the series of experiments with different energy parameters.

Figure 3 shows the XRD diffractograms for powdered products obtained in a series of experiments. Analysis of XRD-patterns allowed establishing that all the powders are characterized by the presence

of 3 main crystalline phases of iron oxide: magnetite Fe_3O_4, hematite α-Fe_2O_3 and epsilon phase ε-Fe_2O_3. For the powder synthesized with the minimum pulse duration t_{pul} = 280 μs, the presence of strong reflections corresponding to the phases Fe_3O_4 and ε-Fe_2O_3 was found. An increase in t_{pul} due to an increase in only the electric capacity leads to a growth of the relative intensities of the ε-Fe_2O_3 reflections.

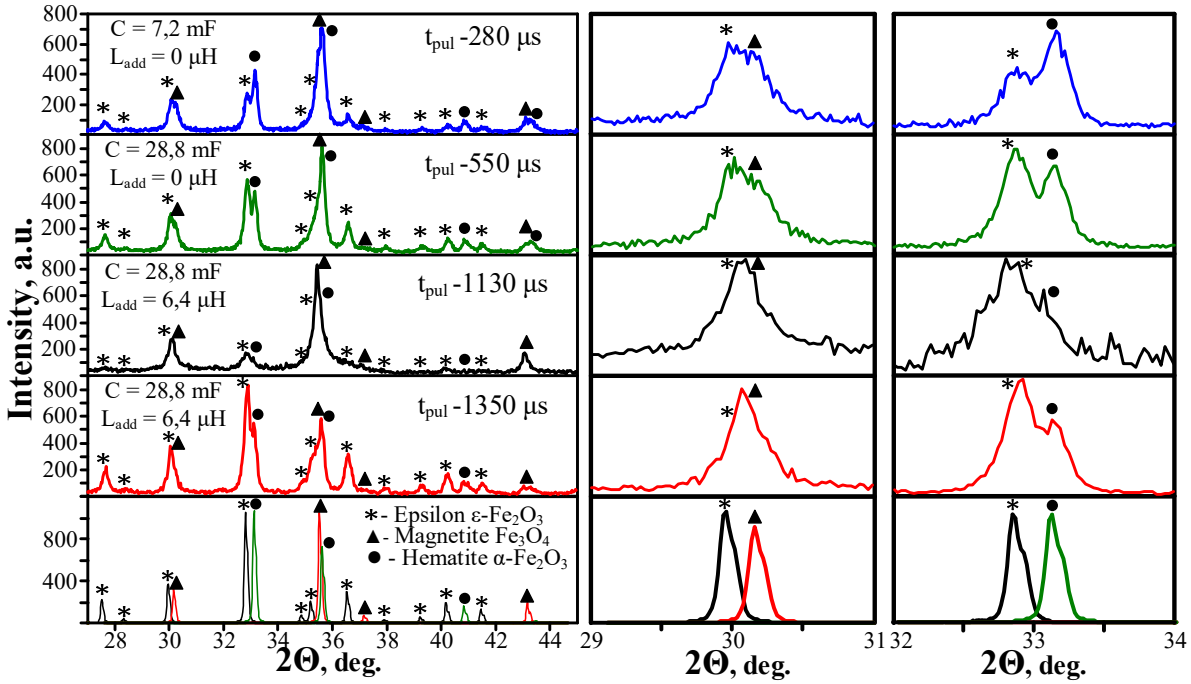

Figure 3. XRD-patterns of synthesized products obtained at different energy parameters.

This is unambiguously confirmed by a change in the numerical estimates of the percentage and the values of the main crystalline lattice parameters as a function of t_{pul} (table 2). With a further increase in the pulse duration due to the introduction of additional inductance, the relative intensities of the ε-Fe_2O_3 reflections firstly fall down at the current amplitude drop (exp. No 4, table 1), and then significantly increase (exp. No. 5). This is also reflected in quantitative estimates of the product composition (table 2). With increase in the pulse duration there is a growth of the average values of the coherent scattering regions (CSR), which can be used for approximate understanding the typical sizes of the particles for every phase.

Comparing the results of estimating the percentage of the main crystalline phases, it can be noted that with an increase in the pulse duration t_{pul} due to a change in the electric capacity, the output of the epsilon phase increases from ~ 30% to ~ 50%. The introduction of additional inductance L_{add} with a slight amplitude of the discharge current (exp. No. 4) adversely affects the output of the epsilon phase, since it is known that when the energy parameters in the considered system decrease, the output of the ε-Fe_2O_3 phase is also lower due to a decrease in the temperature gradient when the material is sprayed from the plasma structure surface [16]. However, a simultaneous increase in the pulse duration and maintaining the amplitude of the discharge current at an acceptable level of more than 100 kA makes it possible to achieve the best results from the position of the ε-Fe_2O_3 phase output up to ~ 65%. This result can be considered as the most optimal, since at lower current amplitude it is possible to achieve a relatively high yield of this unique phase.

Table 2. Results of full-profile structural and phase analysis of products obtained at different t_{pul}.

No. exp. (table 1)	Phase	t_{pul} (μs)	Mass content (wt.%)	Lattice parameters (Å)		CSR (nm)	$\Delta d/d \cdot 10^{-3}$
				Exp.	PDF4		
1	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
2		550	50.1	a: 5.09/b: 8.78/ c: 9.47		43.5	0.6
4		1130	30.0	a: 5.08/b: 8.77/ c: 9,46		48.0	0.2
5		1350	65.0	a: 5.08/b: 8.78/ c: 9.46		56.0	1.2
1	Fe_3O_4	280	45.7	a: 8.37	a: 8.37 a: 8.3750	29.5	1.9
2		550	36.6	a: 8.36		31.0	1.7
4		1130	50.0	a: 8.33		36.0	2.4
5		1350	15.0	a: 8.35		40.0	2.3
1	α-Fe_2O_3	280	23.0	a: 5.03/c: 13.7500	a: 5.0285/ c:13.7360	124.5	1.3
2		550	23.0	a: 5.03/c: 13.7400		104.0	0.3
4		1130	20.0	a: 5.03/c: 13.7100		122.5	1.6
5		1350	20.0	a: 5.03/c: 13.7400		110.0	1.1

4. Conclusion

In this work, several ways to increase the yield and purity of the ε-Fe_2O_3 phase in the system of plasma dynamic synthesis are considered. Based on the well-known Thompson formula for the RLC-circuit, the possibility of changing the pulse duration in the considered system was studied, as well as the effect of this change both on the process energy parameters and the characteristics of the dispersed synthesis products was evaluated. It was established that a change in the electrical capacity of the energy storage device supplying a coaxial magnetoplasma accelerator allows one to increase both the process duration and to obtain a cleaner product from the position of the ε-Fe_2O_3 phase yield. The introduction of additional inductance into the discharge circuit while maintaining an acceptable level of arc discharge current (~ 120 kA) allows not only reducing the dynamic loads in the system, but also increasing the output of the ε-Fe_2O_3 phase up to ~ 65wt. % due to the longer duration of the power supplying pulse. These results can be used to further optimize the considered system for obtaining a unique epsilon iron oxide phase.

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