

PECULIARITIES OF THE OXIDE PLASMA CREATION USING CARBONATE COMPOUNDS

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The process of obtaining oxide plasma from carbonate compounds of calcium CaCO_3 and neodymium $\text{Nd}_2(\text{CO}_3)_3$ was studied. The experiment was carried out on a two-stage plasma source with a reflective discharge. The experiment was conducted with the following parameters: a discharge voltage of 50...150 V, a current of 8...30 A, a magnetic field of 100...200 Oe, the pressure in the vacuum chamber is $3 \cdot 10^{-3}$... $3 \cdot 10^{-4}$ Torr. The ratio of the ionization potentials φ_i and the dissociation energy ε of the oxide components in the plasma was taken into account when selecting materials and analyzing the experimental data. For various conditions of the plasma arc burning, an analysis was made for the composition of the plasma and the elemental composition of the deposited target surfaces based on the experimental data.

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INTRODUCTION

In the articles [1, 2] plasma methods were proposed for reprocessing spent nuclear fuel (SNF). SNF is predominantly an oxide compound of nuclear fuel and decay products. Therefore, the study of the creation features and oxide plasma parameters is of great interest. For the study, calcium oxide (as a representative of alkaline-earth metal oxide) and neodymium oxide (as a representative of oxides of the lanthanide group) were chosen. The creation of an oxide plasma is possible with the direct ionization of the oxides [3] or by affecting the compounds so that the compounds decay and form the oxides. In this paper, the process of obtaining oxide plasma by the action of a vacuum arc on carbonates CaCO_3 and neodymium $\text{Nd}_2(\text{CO}_3)_3$ was studied. The ionization of the oxide occurs in the gas phase. The use of carbonates can significantly reduce the energy input into the discharge since the decomposition temperatures of carbonates are significantly lower than the melting points of the oxides.

PREPARATION AND CARRYING OUT EXPERIMENT

The creation of oxide plasma from carbonates is a difficult problem. It requires an individual approach in each case. The polyatomic nature of carbonate molecules, decomposition temperatures, dissociation energy and ionization energy of both carbonates and their constituent elements must all be taken into account.

Carbonate compounds are mainly represented as crystalline hydrates and are hygroscopic. Neodymium carbonate forms crystalline hydrates: $\text{Nd}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O}$, where $n = 2.5$ and 8. Already at temperatures around 50°C there is an intensive release of water, which greatly complicates the maintenance of vacuum conditions. Therefore, before the experiment, the carbonate powder must be preheated and dehydrated. The heating should be carried out at temperatures not exceeding the decomposition temperature of the carbonate. If the decomposition temperature is

exceeded, an undesirable decomposition of carbonates into oxides will occur [4, 5].

The experiment was carried out on a model of a two-stage source with a reflective discharge [2]. A schematic view of the source is shown in Fig. 1.

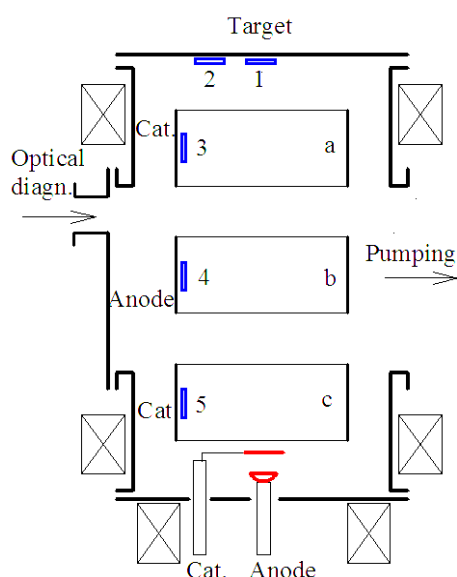


Fig. 1. Two-stage source with a reflective discharge

The choice of materials took into account the ratio of the ionization potentials φ_i and the dissociation energy ε of the investigated oxides. The ratio of ε/φ_i influences on the redistribution of concentrations between ionic components and the mapping of the corresponding lines in the plasma emission spectrum. When $\varepsilon/\varphi_i < 1$ (CaO) – with increasing discharge current the dissociation of the oxides occurs, followed by ionization and appearance of lines in the spectrum corresponding to atomic ions. When $\varepsilon/\varphi_i > 1$ (Nd_2O_3) – ionization of oxides without dissociation occurs together with the appearance of lines in the spectrum corresponding to molecular ions. For uranium oxide, the situation is similar to neodymium oxide.

We can consider two stages of creating oxide plasma from carbonates. The first is the thermal decomposition and evaporation of carbonate dissociation products, the

second is the ionization of vapors and decay products entering the discharge region. In Fig. 2 the thermal decomposition stage of Ca and Nd carbonates is presented [3].

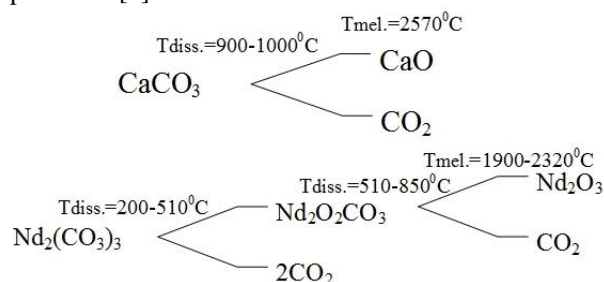


Fig. 2. Thermal decomposition of Ca- and Nd- carbonates

The decomposition of CaCO_3 takes place in one stage at a temperature of $T_{\text{diss.}}=900\dots1000^\circ\text{C}$ with the formation of calcium and carbon dioxide. The decomposition of $\text{Nd}_2(\text{CO}_3)_3$ occurs in two stages. At a temperature of $T_{\text{diss.}}=200\dots510^\circ\text{C}$, neodymium carbonate decomposes into neodymium oxycarbonate and carbon dioxide. At a temperature of $T_{\text{diss.}}=510\dots850^\circ\text{C}$, the

oxycarbonate decomposes into neodymium oxide and carbon dioxide. As a result of decomposition, oxides and carbon dioxide enter the discharge region. In this case, the introduction of oxides into the discharge passes without melting. The melting point for calcium oxide is $T_{\text{mel.}}=2570^\circ\text{C}$, and for neodymium oxide $T_{\text{mel.}}=1900\dots2320^\circ\text{C}$.

DISCHARGE WITH CALCIUM CARBONATE

In Fig. 3 the emission spectra of the plasma of CaCO_3 are shown at discharge currents of 5 A and 10 A. The measurements were performed by the SL40-2-3648USB spectrometer. The decoding of the spectra was made on the basis of [6, 7]. At discharge currents of 5 A on the spectrum (as a result of the shortage of energy introduced into the discharge), the lines of excited singly charged CaII ions are not observed. The spectrum is represented by lines connected with water, hydrogen and other impurities. At discharge currents of 10 A, two lines of singly charged CaII ions (393, 367, 396, 847 nm) and singly-charged CII ions (657.8 nm) appear in the spectrum.

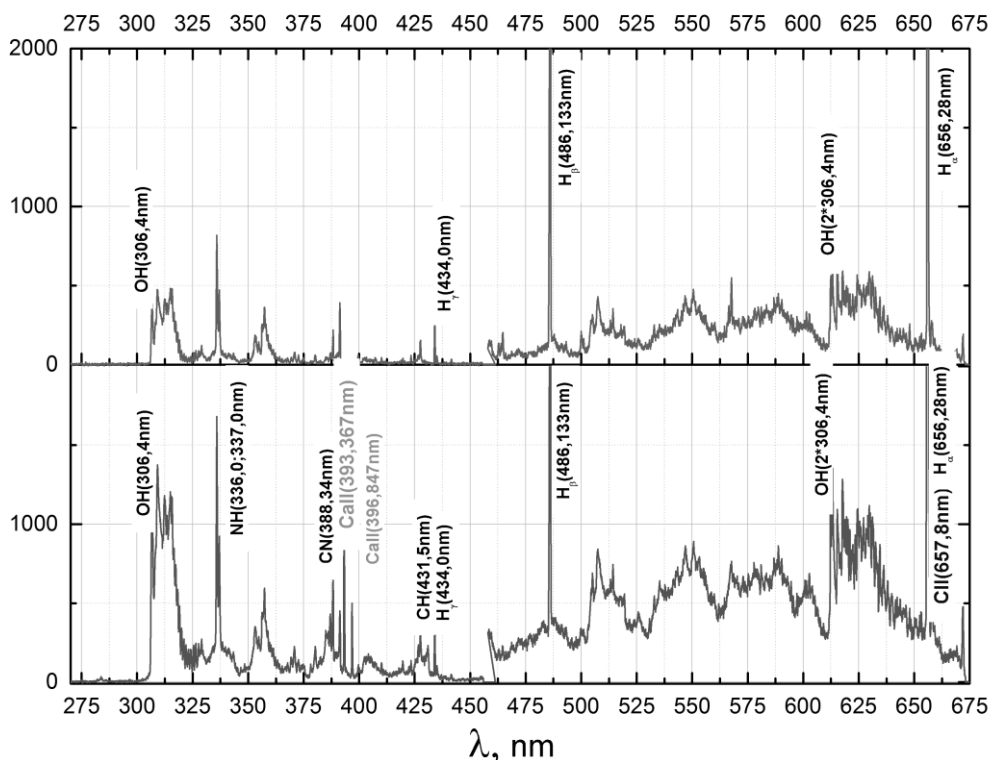


Fig. 3. Plasma spectra at discharged with CaCO_3 : 1 – The upper spectrum. Discharge current $I = 5$ A, voltage $U = 90$ V, pressure $P = 3 \cdot 10^{-4}$ Torr. 2 – Lower spectrum. Current $I = 10$ A, voltage $U = 90$ V, pressure $P = 3 \cdot 10^{-3}$ Torr

In Fig. 4 the spectrum of CaCO_3 plasma at the discharge current of 18 A is shown. The increase in power introduced into the discharge led to an increase in the degree of ionization, a significant decrease in the peaks of water and impurities. The spectrum contains

peaks of singly charged CaII ions (393.367, 396.847 nm) and line of Ca (422.673 nm). The line of C (657.8 nm) is insignificantly traced. If sulfur is present in the carbonate [8], CaII lines are not observed when the discharge current is increased.

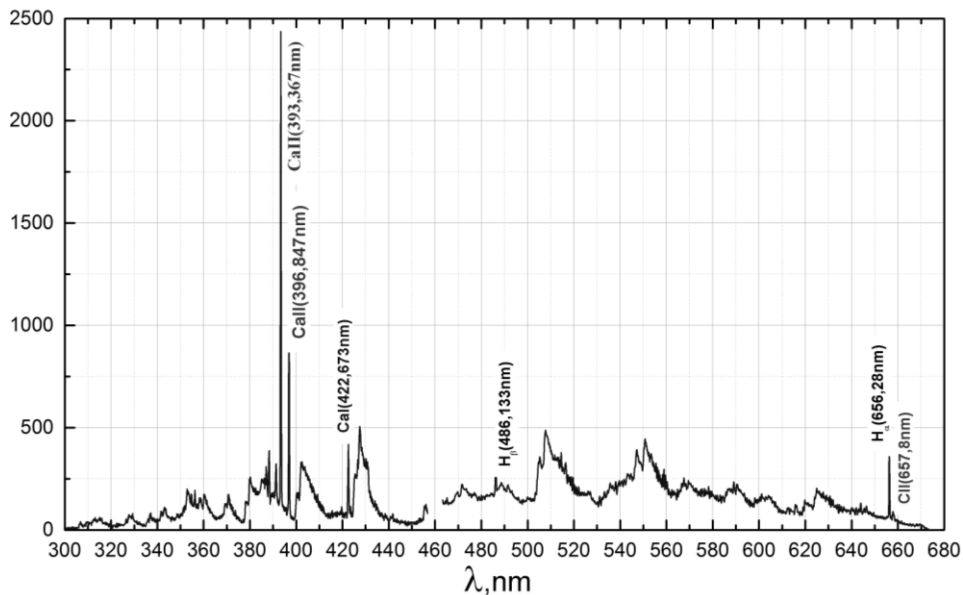


Fig. 4. Plasma spectra at discharged with CaCO_3 . Discharge current $I = 18$ A, voltage $U = 150$ V, pressure $P = 7 \cdot 10^{-3}$ Torr

Figs. 3 and 4 show that an increase of the discharge power leads to an increase in the intensity of the lines of calcium ions with a decrease in the intensity of the lines of the molecular spectrum and carbon lines. This is due to the fact that for calcium oxide $\varepsilon/\varphi_i < 1$. Before the ionization of calcium, energy is additionally expended on dissociation processes, and the number of molecular components in the plasma decreases.

DISCHARGE WITH NEODYMIUM CARBONATE

In Fig. 5 the emission spectra of $\text{Nd}_2(\text{CO}_3)_3$ plasma at discharge currents of 8 and 18 A are shown. As in the spectrum with calcium carbonate, lines with water, hydro-

rogen, and impurities are observed at low discharge currents (8 A). The lines associated with neodymium are absent. When the discharge current increases to 18 A, the intensity of the spectrum increases and lines of singly charged carbon ions CII (5132.94 nm) and CII (5145.16 nm) appear. In the range of discharge currents of 8...30 A, lines connected with atomic neodymium ions are not observed. Since the ionization potential of neodymium oxide is lower than its dissociation potential, neodymium is represented as ionized and excited oxide molecules. For the appearance of neodymium ion lines, a significant increase in the energy introduced into the discharge is necessary. This is due to the transfer of energy to rotational, vibrational levels and dissociative processes.

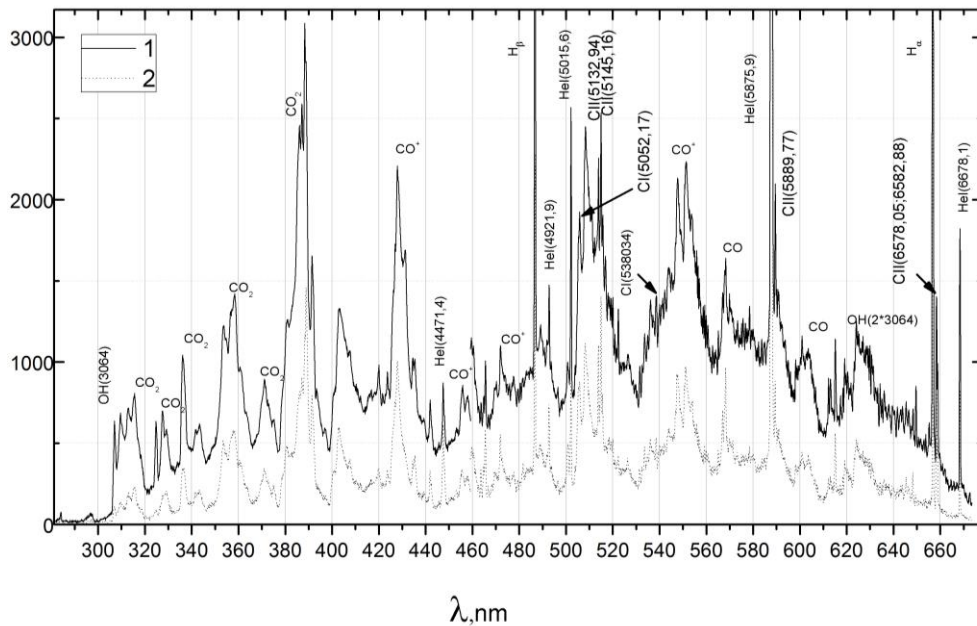


Fig. 5. Plasma spectra at discharged with $\text{Nd}_2(\text{CO}_3)_3$, discharge voltage $U = 150$ V, pressure $P = 5 \cdot 10^{-3}$ Torr, discharge current I : 1...18 A; 2...8 A

The table shows the result of X-ray fluorescence analysis of the surface of five targets (see Fig. 1) after deposition in plasma. Material of the targets is titanium, target number 0 is test. The main quantity of neodymium compounds was fixed on the surface of target number 5, which was located on the reflecting electrode-c. This is because the third electrode was under the potential of the cathode. The motion of ions of neodymium oxide was determined by the electric field, since in this system the magnetic field of 200 Oe could not magnetize them.

Elemental composition of the target surface

Element	Target №0,%	Target №1,%	Target №2,%	Target №3,%	Target №4,%	Target №5,%
Ti ²²	99.902	97.528	99.799	99.523	99.092	93.904
Fe ²⁶	0.0775	0.0793	0.0252	0.0726	0.0185	0.0483
Ni ²⁸	0.0200	0.0135	0.0070	0.0162	0.0078	0.0286
Cu ²⁹	—	0.5955	—	0.3123	0.1535	0.3729
Nb ⁴¹	—	—	0.0045	—	—	—
Mo ⁴²	—	0.0189	0.0040	0.0027	0.0100	0.0928
Nd ⁶⁰	—	1.702	—	—	0.4447	4.192
Ta ⁷³	—	—	0.1006	—	—	—
W ⁷⁴	—	0.0509	0.0193	0.0629	0.2675	1.2990

CONCLUSIONS

When preparing the creation of a discharge, it is necessary to take into account the temperatures of dehydration and decomposition of carbonate compounds. The plasma composition depends on the ratio of the ionization potential and the decomposition energy. Elemental analysis of the targets surface, located in different places of the discharge chamber indicates the presence of ionized neodymium oxide in the discharge.

ОСОБЕННОСТИ СОЗДАНИЯ ОКСИДНОЙ ПЛАЗМЫ ИЗ КАРБОНАТНЫХ СОЕДИНЕНИЙ

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Исследовался процесс получения оксидной плазмы из карбонатных соединений кальция CaCO₃ и неодима Nd₂(CO₃)₃. Эксперимент проводился на двухступенчатом источнике с отражательным разрядом. Напряжение разряда 50...150 В, ток 8...30 А, магнитное поле 100...200 Э, давление в вакуумной камере 3·10⁻³ ...3·10⁻⁴ Торр. При выборе материалов и анализе экспериментальных данных учитывалось соотношение потенциалов ионизации φ_i и энергии диссоциации ε оксидных компонент в плазме. На основании экспериментальных данных для различных условий горения плазменной дуги сделан анализ состава плазмы и элементного состава напыленных поверхностей мишеней.

ОСОБЛИВОСТІ СТВОРЕННЯ ОКСИДНОЇ ПЛАЗМИ З КАРБОНАТНИХ З'ЄДНАНЬ

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Досліджувався процес отримання оксидної плазми з карбонатних з'єднань кальцію CaCO₃ та неодиму Nd₂(CO₃)₃. Експеримент проводився на двоступінчатому джерелі з відбивним розрядом. Напруга розряду 50...150 В, струм 8...30 А, магнітне поле 100...200 Е, тиск у вакуумній камері 3·10⁻³...3·10⁻⁴ Торр. При виборі матеріалів та аналізі експериментальних даних враховувалося співвідношення потенціалу іонізації φ_i та енергії дисоціації ε оксидних компонент у плазмі. На підставі експериментальних даних для різних умов горіння плазмової дуги зроблено аналіз складу плазми і елементного складу напилених поверхонь мішеней.

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