

Novel DC arc plasma method for super dispersed metal carbides synthesis

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Abstract. This paper presents the experimental results of metal carbides synthesis by DC arc discharge plasma in ambient air. The results indicate that the synthesis takes place in the atmosphere of CO and CO₂, which are generated during the DC arcing process on graphite electrodes and that mixture of CO and CO₂ prevents the reaction zone from air oxygen. The paper introduces experimentally substantiated arguments about the possibility of obtaining metal carbides by the developed arc discharge method. By the moment, the authors have already obtained silicon carbide and titanium carbide in this way.

1. Introduction

Metals and non-metals carbides play a significant role in the scientific and technical development for over 100 years [1]. The scientific community pays much attention to some carbides due to their outstanding properties, such as superhardness, refractoriness, wear resistance, resistance to aggressive media, catalytic activity, etc. In this regard, the number of publications devoted to the carbides synthesis and study of their properties has increased significantly over the past 20 years (Figure 1). The most studied carbides are silicon, boron, tungsten, and titanium carbides, while at the same time more rare carbides are known, such as platinum, palladium, yttrium, uranium, beryllium, cerium, ruthenium carbides, etc. To date, carbides are usually prepared by carbothermic reduction of oxides in furnaces of various types: generation of electron and ion beams, generation of electric discharge and microwave plasma, chemical vapor deposition (CVD), laser ablation, etc. All existing methods are generally implemented in inert gas or liquid, preventing the synthesizing product from air oxidation. At the same time, in the last 5–8 years, there have been some papers in the scientific literature about the possibility of synthesizing carbon nanotubes and graphene by electric arc plasma in the air [2–4], including ambient air [5, 6]. This approach allows significantly simplify the design of electric arc plasma reactors and reduce the cost of carbon nanostructures synthesis [4]. By this moment there is the substantial experience of carbon nanotubes electric arc synthesis by such approach [7]. However, the metal carbides synthesis by electric arc plasma in ambient air practically has not been studied. In particular, the following issues are not resolved: a list of materials, which can be synthesized by such method; an actual gas composition in a reaction zone; operating parameters of a discharge circuit and current-voltage characteristics of arc discharge, which are required to obtain the desired material. Experimental studies with control of electrical parameters of the discharge circuit, the electrodes temperature, and the gas atmosphere can only partially solve the above-mentioned issues.

This paper represents the experimental studies showing the possibility of metal carbides synthesis by DC arc discharge plasma in ambient air. In this case, a DC arc discharge is initiated in the cavity of a graphite crucible, into which a mixture of metal and graphite is placed. The qualitative assessment of



the gas composition during the experiments is presented. This result showed that, in fact, synthesis takes place mainly in the atmosphere of CO and CO₂. The data presented in conjunction with our previous papers [8–10] suggest that the synthesis of metal carbides by the non-vacuum method being developed is possible.

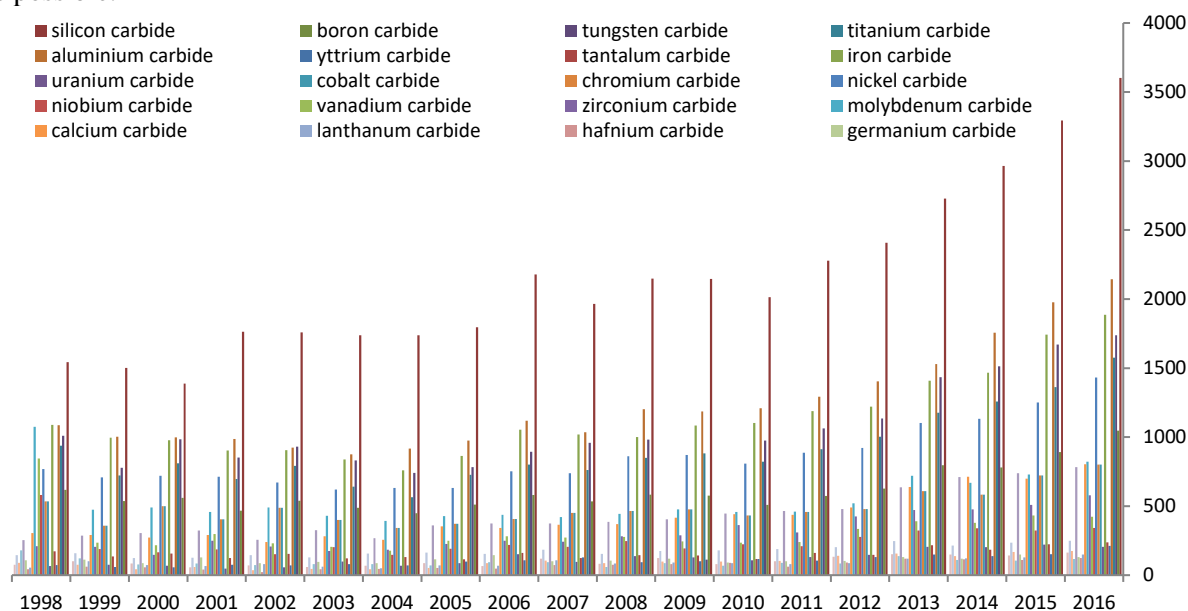


Figure 1. Dynamics of publication activity on metals and non-metals carbides according to sciencedirect.com.

2. Experimental methods

Experiments were carried out using a DC arc discharge reactor (Figure 2) that was created by the authors of this paper [8]. It included graphite electrodes connected to the DC power source. The power source consists of a step-up frequency converter, a step-down transformer, and controlled rectifier. The anode was a graphite cylindrical rod; the cathode was a graphite crucible, filled with a powder mixture of some metal and graphite. In this series of experiments, graphite rods with a diameter of 8 mm were used as anodes; graphite crucibles with a diameter of 30 mm and a height of 30 mm – as the cathodes. The anode and cathode were weighed before and after each experiment. The arc discharge gap was controlled during the experiment by a linear electric drive based on a stepper motor, which was operated by the driver and controller. The arc current and the voltage on the electrodes were recorded using a two-channel oscilloscope through an ohm voltage divider and a current sensor (Hall Effect sensor). The electrodes temperature was controlled by a pyrometer. The gas composition was determined by a gas analyzer, the probe of which was located directly above the arc zone at a distance of about 10 cm. The arcing was generated by a voltage of 30–35 V with DC of 160–170 A.

The general principles of operation of the electric arc reactor being developed and the possibility of synthesizing silicon carbide and titanium carbide by DC arc discharge plasma in ambient air have already been discussed previously [9,10].

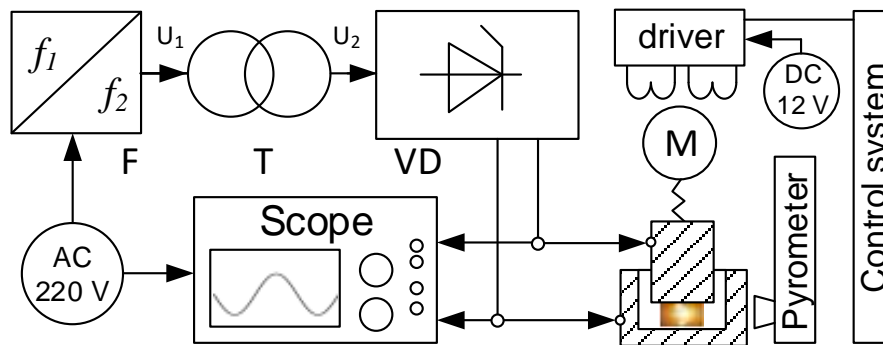


Figure 2. Schematic diagram of the experimental setup.

3. Results and discussion

Figure 3 shows the detected dependencies as a result of a series of experiments in which the duration of arc discharge was varied with constant parameters of the discharge circuit and the current-voltage characteristics. As can be seen from Figure 3a, the arc energy grows with increasing synthesis time almost linearly. The energy release lead to the temperature rise in the system, including on a cathode surface (Figure 3b). As is evident, the temperature of the cathode surface increases to approximately $\sim 1100\text{ }^{\circ}\text{C} - 1200\text{ }^{\circ}\text{C}$ over a 20-second interval of the reactor operation. A time of $\sim 15\text{--}20$ seconds should be considered as the limit for the operation of the reactor without a cooling system since the graphite cathode begins to ignite in the open air. The amount of energy, released during this time in the system, is up to $\sim 60\text{--}100\text{ kJ}$.

Figure 3 also presents the dependencies between the anode mass loss (Figure 3c) and the mass of cathode deposit (Figure 3d), formed during the arcing process, with the synthesis time. The process of mass transferring from anode to cathode with the formation of a cathode deposit is known [7]. In the considered series of experiments, it is clear that as the duration of the synthesis increases, both the anode mass loss increases and the mass of the formed cathode deposit increases, which is logical. In this case, we can see that the anode mass loss is greater than the cathode deposit mass. It indicates that the part of the anode mass is expended on a gaseous product formation.

Gases, formed during the operation of a non-vacuum electric arc reactor, were determined by the gas analyzer. The results of gas analysis should be considered qualitative due to the lack of a hermetic reactor as part of the experimental setup. Nevertheless, the obtained results seem logical.

The formation of CO and CO₂ is uniquely identified as a result of the arc discharge initiation. These gases are products of graphite electrodes combustion when arc discharge initiating and maintaining. As can be seen from Figure 4, the gas analyzer recorded the release of CO and CO₂ gases at different points in time. Unfortunately, we could not synchronize the time of the gas appearance with oscillograms of the reactor operating mode, since it takes some time for the gas to path from the probe to the detector. Nevertheless, the difference in the appearance of CO and CO₂ gases is present in all experiments: first appears CO₂, then CO. At first, oxygen reacts with carbon atoms to form CO₂, and then CO₂ reacts with carbon atoms to form CO [11]. A similar phenomenon is also described in [12] when discussing the four stages of the electric arc process for the silicon carbide synthesis. The synthesis of silicon carbide takes place in a reactor, filled with He, with the CO and CO₂ formation when treated silicon dioxide SiO₂ with carbon plasma. In addition to CO and CO₂, the release of a small amount of hydrogen H₂ was also recorded, which generation often accompanies plasma processes [13,14], and specifically, in this case, it may be the result of the presence of atmospheric humidity and adsorbed moisture in the consumables used. Hydrogen, in turn, is actively used as the atmosphere for electric arc reactors (for example, in [15]), respectively, its presence or absence in the system under consideration is not critical.

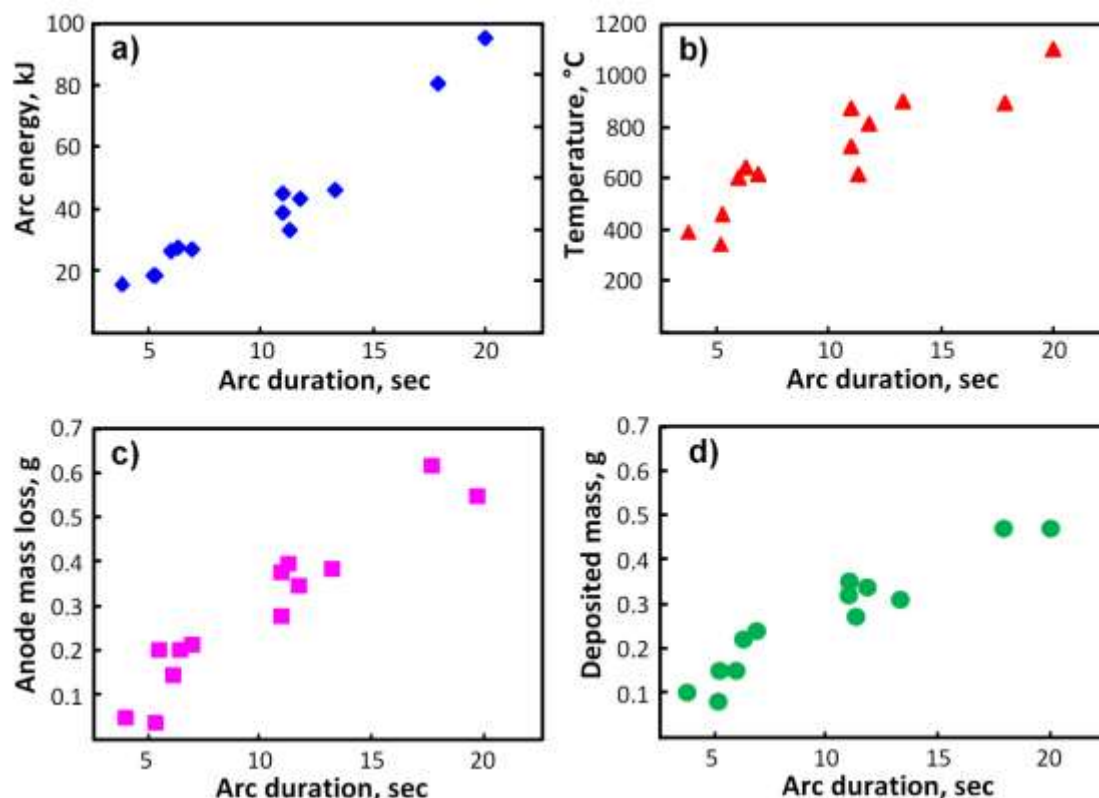


Figure 3. The dependencies between the arc energy (a), the temperature of cathode surface (b), the anode mass loss (c), the cathode deposit mass (d) with the arc duration in a series of experiments.

The obtained result is verified by known data. The possibility of carbon nanotubes synthesis by the arc method in the CO atmosphere is proved [16]. It is also known, that the carbon nanohorns synthesis is possible both in the CO, CO₂ atmosphere, and in ambient air, due to the CO generation [11]. Thus, it is safe to conclude that non-oxide materials can be synthesized by DC arc discharge plasma on graphite electrodes by creating the atmosphere of CO and CO₂. In addition, according to the literature data, oxygen in SiO₂ composition is replaced by carbon atoms in the synthesis process, oxygen combines with carbon and the synthesis of CO and CO₂ occurs during the SiC synthesis from SiO₂ by DC arc discharge plasma in He atmosphere [12]. So, it means the atmosphere in the synthesis process mainly consists of CO and CO₂, both in the case of arc discharge initiation on graphite electrodes in air and inert gases (in the case of the oxygen's presence in the precursor). This means that the presence of a sealed chamber in the reactor is not critical for the synthesis of powder materials by DC arc discharge plasma initiated between graphite electrodes. Since, in any case, oxygen will be in a bound state in the composition of CO and CO₂ during the synthesis process

This principle made it possible to realize the synthesis of silicon carbide and titanium carbide [8–10] by DC arc discharge plasma, initiated on graphite electrodes, in ambient air. This proves the consistency of the above theses. Moreover, according to the well-known state diagrams [17], many metal carbides are formed under relatively similar conditions (in particular, in the temperature range from 1000 °C to 4200 °C). Many materials have already been obtained by the traditional electric arc method in a sealed reactor in the inert atmosphere. Taking into account the carried-out research, it seems possible to synthesize such materials by the non-vacuum method. Accordingly, in addition to the silicon carbide and titanium carbide, that have already been synthesized by the non-vacuum method being developed [8–10], it is also possible to synthesize tungsten, molybdenum, lanthanum, yttrium, zirconium, chromium, and other metals carbides. Thus, the task of future research is to synthesize of the mentioned-above carbides by the non-vacuum method. As evidence of the above assumptions, in the papers [8–10]

the results of X-ray diffractometry and electron microscopy are presented. The results in these works indicate that the titanium carbide and the silicon carbide were synthesized and that there was not silicon and titanium oxide in the product.

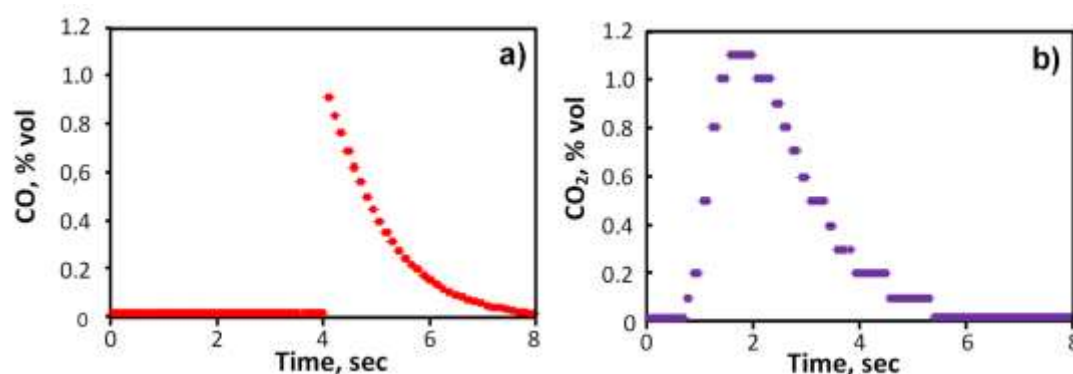


Figure 4. Typical changes in the concentration of carbon monoxide (a) and carbon dioxide (b) during the experiment.

4. Conclusion

The paper presents systematically collected data for the process of electric arc synthesis of powder materials by DC arc discharge plasma in ambient air. As part of the non-vacuum method development, the assessment of the actual gas atmosphere was carried out. For the first time, it was experimentally substantiated that the electric arc synthesis of metal carbides can be implemented in ambient air without a sealed chamber and vacuum equipment. The synthesis process is possible as a result of CO and CO₂ generation during the arcing process on graphite electrodes.

Acknowledgment

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