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ABSTRACT

Pulsed anodic arc discharge is a novel synthesis method of nanomaterials by means of low-temperature atmospheric plasma. The technique consists in periodically supplying DC power to two vertically aligned electrodes in the form of short unipolar pulses with peak currents of a few hundred Amperes in a helium atmosphere. The pulsed arc plasmas are sustained at frequencies on the order of 1 Hz with around 10% of duty cycle. It constitutes a versatile technique thanks to a series of advantages compared to continuous DC arc processes, in particular, flexibility in the experimental conditions, process stability and repeatability, better utilization of ablating anode material, lower production of macroparticles, and lower thermal loads. Such features are discussed in this article. A brief overview concerning the recent accomplishments of pulsed arc discharge on deposition of carbon nanostructures (graphene and carbon nanotubes) and few-layer flakes of molybdenum disulphide and an outlook on future applications of this method for the discovery of new materials with tailored functional properties are provided.

Anodic arc discharge constitutes a versatile technique to synthesize low-dimensional nanostructures, such as nanotubes and 2D flakes, from the evaporation of an anode acting as a solid precursor.[1–5] Investigation of nanomaterial synthesis by atmospheric arc discharge is a relevant research field because it can provide the answer to the general question of what pressure, gas composition, and temperature are suitable to nucleate particles from ensembles of neutral species and ions in the plasma state. The material evaporated in arc discharges is known to enable a rich environment of gas species with extended gradients of plasma densities and gas temperatures adequate for growth of particles of different sizes. Proper values of arc voltage and arc current are easily set in the plasma arc system, which confers an incomparable flexibility to the growth process especially convenient for exploring the correlation between synthesis parameters and nanoparticle characteristics. Thus, arc discharge experiments provide benchmarks to understand the physics of nanosynthesis in the plasma phase, which, in turn, serve to optimize recipes of nanomaterial growth by other physical or chemical vapor deposition techniques.

Recent challenges in the volume synthesis of new nanomaterials have required the exploration of further arc growth recipes besides standard DC arc discharge conditions.[6] Earlier, the need of depositing thin films or coatings with especially tailored properties emerged in the field of surface synthesis methods, such as pulsed cathodic arc discharge,[7] pulsed DC plasma vapor deposition,[8,9] and, more recently, high power impulse magnetron sputtering (HiPIMS).[10,11] All these techniques are characterized by the periodical excitation of cold plasmas by means of short intense pulses. Whether discharges remain ignited or experience periodical extinctions and afterglow regimes, such plasmas are sustained far from the steady state but in a transient regime, showing periodical changes in plasma parameters and sheath dynamics.[12] There are already published reports on pulsed arc discharge to grow carbon nanostructures and ceramic coatings with pulses within the kHz range.[4,13,14] The use of middle-high frequencies is needed to hinder the runaway of hot electrons confined in the plasma volume between two consecutive pulses. Recently, pulsed arc discharges on graphite anodes were reported to be held within the frequency interval of 1–5 Hz with duty cycles of 10% (respective pulse durations: 100–20 ms).[6,15] The relatively slow and stable pulsed arcs were feasible thanks to the special design of the discharge current waveform, which is described below. It has been observed that pulsed arc discharges are characterized by providing single bursts of intense arc current without modifying the basic plasma processes that are characteristic of nanoparticle production from DC arc plasmas.[6]

The present article is intended to outline the key features of pulsed anodic arc discharges in view of their immense potential to generate new nanostructured materials. Here, we summarize and

discuss the main characteristics of anodic arc discharges subjected to periodic unipolar pulses in a Helium atmosphere aimed to nanomaterial growth. Such an approach to pulsed arc plasmas is necessary and has not been performed before. In the following paragraphs, we describe the main defining parameters of pulsed anodic arc discharge and compare the main features of such discharge with usual performance of DC discharge.

A clear advantage in anodic arc experiments, in contrast to other plasma types such as glow discharges, is a possibility to control basic discharge features through a few technological parameters. Arc voltage and arc current can be set independently, both being critical for specific discharge characteristics. In general, discharge voltage should be a few times higher than ionization energy of the gas species, E_i, in order to enhance ion and electron generation. For example, arc voltages of approximately 20–30 V suffice to run an arc discharge supported by carbon atoms ($E_i = 11.3$ eV).[16] On the other hand, total arc currents (ionic plus electron current) of around 50 A provide a power density high enough to support anode erosion and particle synthesis.[3] The increase in gas pressure will partially diminish gradients of particle density and of gas temperature thanks to an enhanced gas diffusivity. Also, drift current (due to the electric field) of charged species in the arc column will be balanced by the diffusion component as pressure increases.[17] In the cases shown in the present paper, the background pressure of He has been set to 300 Torr. Finally, the use of a reactive gas is necessary to synthesize some compounds. For example, boron nitride nanoparticles have been produced in a boron anodic arc experiment with a nitrogen atmosphere.[18]

The arc discharge variables listed above should be conveniently manipulated to render periodic waveforms of arc current and voltage. To this end, a current-controlled DC arc power supply is remotely operated by the pulse signal sent from an external function generator. The main pulse parameters are identified in Fig. 1, and their typical ranges are listed below:

- Frequency: Operation within the range of 1–10 Hz is adequate to obtain stable and reproducible arc pulses. The selection of such a range is intrinsically related to the architecture of the power supply. Indeed, its value must be compatible with the electronic circuitry of the power supply, which consists often of an arc welder operated at a current of 50 or 60 Hz. While the upper limit of pulse frequency is fixed by the frequency of the electrical network or the frequency limit of the source itself, there are, in principle, no restrictions concerning the lower limit of pulse frequency (long pulse period).
- Duty cycle: The adequate pulse duration, T_{on}, is a trade-off between the current rise time and the time to reach DC arc regime. Its value is limited on the lower side by the characteristic rise time of arc current. Such a rise time, T_{rise} (Fig. 1), is determined by the response time of the transformer built in the power supply. On the upper side, the pulse duration is restricted by the transition to the DC anodic arc regime, which takes place within ≈1 s after the pulse is initiated. Such transition is characterized by a migration of the arc core from the interelectrode gap region (breakdown state) to the sidewall of the anode top surface (stationary arc state).[6]
- Amplitude: The maximal arc current, $I_{arc,ON}$, and arc voltage, $V_{arc,ON}$, can exceed the typical values used in standard DC arc processes as long as the average power driven to the plasma remains within the same order of magnitude. For example, synthesis of carbon nanotubes and graphene nanoplatelet networks by DC arc discharge optimized at around 75 A can be upgraded to pulsed processes with peak current topping around 300 A.[6]

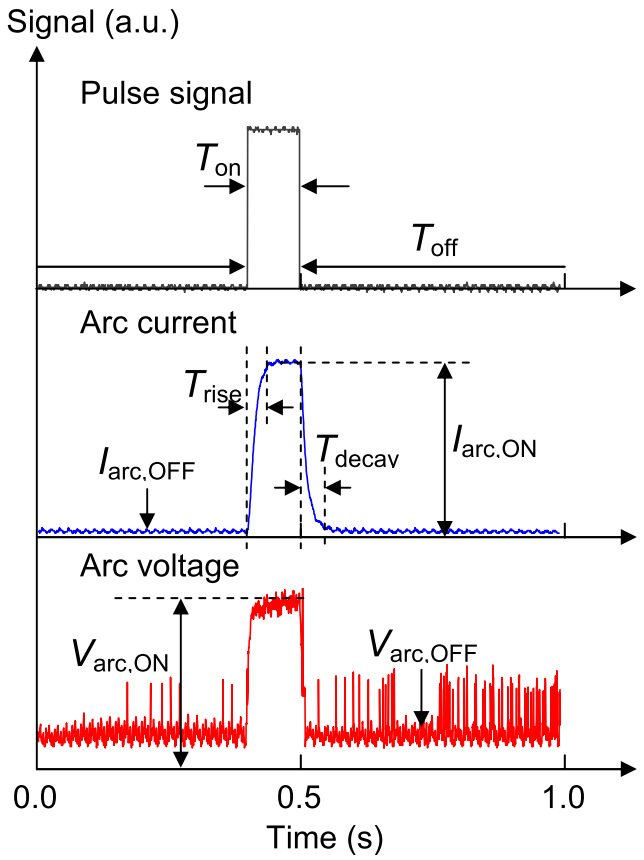

FIG. 1. Identification of the main pulse parameters in the periodical waveforms of (a) voltage of 1 Hz-pulse signals (10% duty cycle) programmed in a function generator and sent to the power supply; (b) arc current, which is proportional to pulse signal voltage and is measured with a current clamp, and (c) arc voltage measured at the interelectrode gap. Duty cycle $= T_{on}/(T_{on} + T_{off})$; $T_{rise} \approx T_{decay}$. All waveforms are recorded using an oscilloscope.

The main features of pulsed anodic arc discharge are discussed below.

While DC arc discharges are mostly active on top and around the anode in an irregular and unpredictable manner, arc discharge pulses show maximal optical emission during the ON phase preferentially at the gap defined between the anode and the cathode (Fig. 2). The periodical action of pulsed power promotes a remarkably stable discharge, thereby providing repeatable synthesis processes. Hence, pulsed arcs perform in contrast to continuous DC arcs. The latter are characterized by erratic dynamics of the arc core caused, for instance, by anode attachment instability, which can be ascribed to unpredictable oscillations of the arc voltage.[19,20] Such instabilities might have an impact likely on erosion dynamics as judged from the irregular anode tip shape commonly observed after continuous DC arcs. Pulsed arcs can address this shortcoming and constitute a practical alternative to other

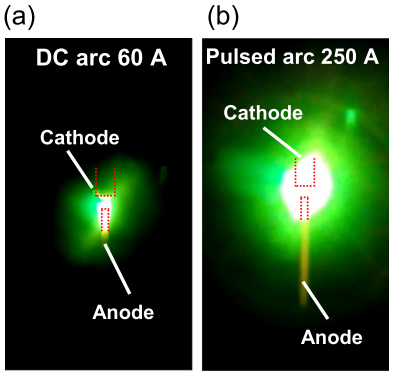

FIG. 2. Images of (a) DC arc held at 60 A (suitable for carbon nanoparticle growth) and (b) ON phase of the pulsed arc held at 2 Hz, 10% duty, and $I_{arc,ON} = 250$ A (also providing nanoparticle-rich samples) between graphite electrodes. The pulse parameters are chosen so that peak current is the maximal attainable value and the duty cycle is long enough to reach (or approach) the plateau current and yet short enough to preserve the integrity of the anode. The positions of the electrode edges are indicated with red dotted lines. The arc discharge images were recorded using a digital camera (≈10 frames/s). A filter strongly absorbing in the visible range was installed on the view port to attenuate the intense optical emission from the anodic arc discharge.

arc stabilization strategies, as, for instance, introduction of magnetic fields aimed to steer and homogenize the path of the arc column.[2,21]

Figure 3 shows the qualitative potential evolution along the interelectrode gap. The regions attributed to plasma sheaths and to the arc column are indicated together with their respective voltage drops. The region of high arc current plateaus in the carbon arc current waveform, also called the ON period, was characterized by high plasma density ($>3 \times 10^{22}$ m^{-3}).[15] Such a region was followed by a less active, OFF period, where the arc discharge is in the latent state ($I_{arc,OFF} \approx 10$ A or less). As studied elsewhere,[15] the discharge does not

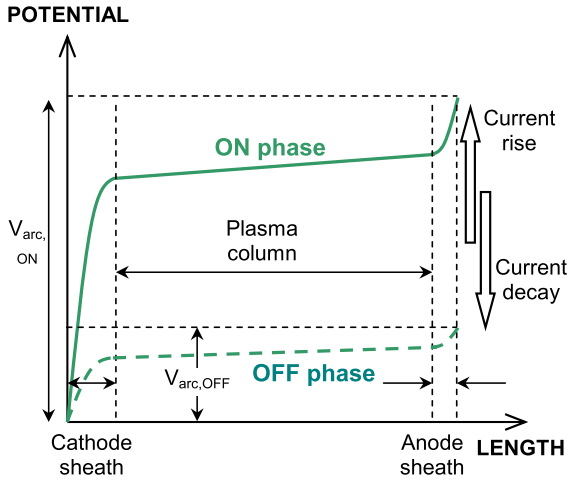

FIG. 3. Schematic evolution of the electrostatic potential along the interelectrode gap in the ON and OFF phases during pulsed arcs. The respective arc voltages are $V_{arc,ON}$ and $V_{arc,OFF}$. At low arc currents, the anode sheath can undergo transition into an ion attracting sheath.[17]

vanish, but it remains in a less active state that can be identified as a constricted arc with non-zero finite arc voltage ($V_{arc,OFF}$). Its plasma density is substantially lower than that in the ON phase. The estimation of such a plasma density value is described in the supplementary material. In addition, a video showing a constricted arc sustained between graphite electrodes after undergoing a series of arc pulses (2 Hz, 10% duty) is posted in the supplementary material to illustrate its localized and relatively weak optical emission. The fact that the pulsed discharge never extinguishes plays in favor of the synthesis process stability.

Evaporation of the solid anode takes place thanks to the streaming electrons and the elevated gas temperatures promoted by the arc plasma. Thus, the anode is preferentially eroded in or near the hottest regions of the discharge. A consequence of the dominant central location of the arc core in pulsed discharge is the selective erosion of the topmost anode area due to the major thermal energy density concentrated in such a zone. This "chopping" phenomenon, which leaves flat-ended anodes after pulsed plasma operation, contrast with the more irregular erosion characteristic of continuous DC arc discharge.[6] The latter leaves rounded, irregular tips on the anodes because of important erosion of the anode sidewall associated with anode arc attachment in this area. The sketches in Fig. 4(a) show graphically the modeled erosion as a function of the arc mode. Such distinction between irregular and chopping ablation mechanisms is advantageous for anode reutilization and selective evaporation in compound anodes. For example, molybdenum disulphide (MoS_2) has been synthesized in monolayer flakes by exciting a pulsed arc discharge that evaporated micrometer-sized MoS_2 powder lodged in a hollow graphite anode.[22] Figure 4(b) shows the top view of such a compound anode, filled with MoS_2 powder, before and after pulsed arc evaporation. Note the powder depletion due to preferential near-axis erosion. Large powder depletion of the hollow anode and marginal ablation of the graphite container are associated with MoS_2 monolayer production with a moderate carbon content.[22]

The mixture of synthesized nanomaterials with macroparticles is an important issue in arc discharge. For instance, the co-synthesis of amorphous carbon-containing powder has been identified as a significant side process in graphite ablation by arc plasma.[23] Such a phenomenon can be correlated with a decrease in the chamber pressure. Indeed, the density of gas species decreased due to depletion of carbon atoms in the vapor phase, which contributed to macroparticle growth by means of their nucleation and ulterior coagulation in carbon aggregates. In summary, pressure variation permits us to monitor the growth rate of carbon macroparticles. It was demonstrated recently that the undesired generation of carbon powder was minimized in pulsed arc processes since the pulse duration was too short to trigger steady powder formation.[6] Consistently, the working pressure in the pulsed regime on the graphite anode did vary with small oscillations (50 Torr peak-to-peak) held at the pulse frequency, in comparison with the larger pressure variations characteristic of continuous DC arcs (up to few hundred Torr). Similarly, small pressure variations have also been observed in the synthesis of MoS_2 nanoparticles, which indicates very little macroparticle production for this material as well. Pulsed arc discharge is, therefore, a process confined in the very initial stage of anode ablation with marginal production of macroparticles, thereby increasing material purity. Moreover, control over the 2D interlayer thickness and crystal domain size can be probably improved through the pulse duration.

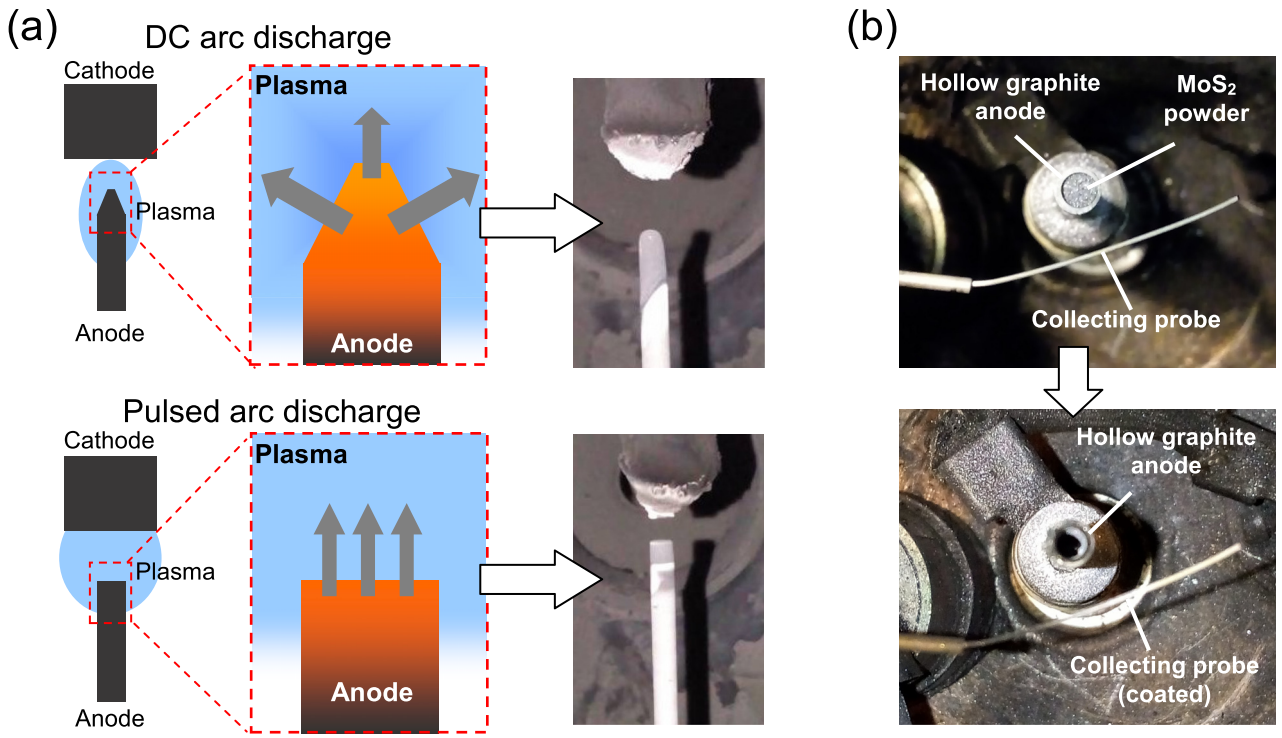

FIG. 4. (a) Modeled ablation processes during DC and pulsed (ON phase) arcs. The gray arrows represent the flux of ejected material. The pictures correspond to solid graphite anodes (3 mm in diameter) after arc discharges. (b) Top view of a compound anode (5 mm in diameter) consisting of a hollow graphite electrode filled with MoS_2 powder before (top) and after (bottom) pulsed arc discharge held at 2 Hz, 10% duty cycle.

The consumed power value is intrinsically connected to the shapes of voltage and current waveforms supplied to the arc plasma system. The product of both curves provides the curve of instantaneous power, whose integral over one pulse period is equal to the average power per pulse. The power associated with pulsed arc plasmas is around 1 kW, while the one used for DC arc discharge processes reaches 2 kW. At the same time, ablation rates of pulsed and DC discharges are 1 mg/s and 2 mg/s, respectively, thereby maintaining ablation efficiencies within the same order of magnitude in both modes (3–4 g/kWh).[6] Nevertheless, net production of nanoparticles is improved in pulsed arc discharge compared to DC arc discharge as outlined above because the latter displays a strong production of powder material (amorphous carbon). The development of sustainable processes is a priority in cutting-edge research toward economical production of nanomaterials.

The temperature at the external wall of the arc chamber was measured using a thermocouple placed at the height of the interelectrode gap and buried with few layers of aluminum foil. The wall temperature during 60 A-DC arc discharge raised at a steep rate of 2.5 °C/s for the whole discharge experiment, surpassing 140 °C by 50 s of operation. In contrast, pulsed arc processes yielded a smoother temperature increase with saturation at ≈55 °C within the same time interval (see the supplementary material). The lower thermal load in pulsed arcs is basically linked to: (1) lower characteristic power values, as mentioned above, and (2) more efficient heat dissipation thanks to the interplay between the gas residence time (here ≈ 10 s) and the pulse duration. However, a detailed analysis of the involved heating mechanisms would require simulation of the conduction and convection fluxes in the arc chamber. An additional heating source to the chamber walls in continuous DC arcs might consist of the generated macroparticle flux, which could contribute to the wall temperature increase via enhanced thermal conduction. Arc processes held at lower gas temperatures are preferred since their employment extends the lifetime of the chamber circuit elements and permits coating of temperature-sensitive substrates.

In conclusion, here, we have listed the main signatures of anodic arc discharges conducted in pulsed mode, showing their adequacy for improving nanosynthesis of new materials. By varying peak current, one modifies the ionization degree, which can approach unity at large enough current values. The accurate selection of the pulse duration (duty cycle) will have a strong influence on the average particle size because the nucleation and coagulation times depend on the time in which energy is driven uninterruptedly to the discharge. The chopping effect of successive pulsed discharges has a beneficial effect on the geometry of ablated anode. Indeed, maintaining the top surface flat during the whole pulsed arc experiment enables more stable erosion processes than in the ablation processes by DC arc discharges, where the top surface adopts irregular shapes due to the random arc core pathway. This effect will be used to synthesize compounds of new materials by selective evaporation of heterogeneous (multi-element) anodes. Finally, the right balance between pulse frequency and the duty cycle is the key to achieve high production rates yet with

moderate gas temperatures that will diminish the aging of the electric components built in the arc chamber. All the points raised above highlight many advantages of pulsed anodic arc discharge, which shows huge potential toward the arc generation of new nanomaterials with tailored properties by means of yet more sustainable and economical processes.

See the supplementary material for (1) the evaluation of electrical parameters of a constricted arc (OFF phase); (2) the heating curves of the chamber wall during arc discharges; and (3) a video showing pulsed arc plasma followed by a constricted arc.

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