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Macroparticle generation in DC arc discharge from a WC cathode.

Igor Zhirkov,^{1,a} Peter Polcik,² Szilard Kolozsvári² and Johanna Rosen¹

¹ Thin Film Physics Division, Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden

² Plansee Composite Materials GmbH, Germany

Abstract

We have studied macroparticle generation from a tungsten carbide (WC) cathode used in a dc vacuum arc discharge. Despite a relatively high decomposition/melting point (~ 3100 K), there is an intensive generation of visible particles with sizes in the range 20-35 μm . Visual observations during the discharge and scanning electron microscopy of the cathode surface as well as of collected macroparticles indicate a new mechanism for particle formation and acceleration. Based on the W-C phase diagram there is an intensive sublimation of carbon from the melt resulting from the cathode spot. The sublimation supports the formation of a sphere, which is accelerated upon an explosion initiated by Joule heating at the critical contact area between the sphere and the cathode body. The explosive nature of the particle acceleration is confirmed by surface features resembling the remains of a splash on the droplet surface.

^aCorresponding author: igozh@ifm.liu.se, phone +46 730 52 10 12, fax +46 13 137568

INTRODUCTION

Tungsten carbide is one of the hardest man-made materials. In its most basic form, tungsten carbide is a fine powder, which can be pressed and formed into required shapes. An efficient way of reducing the cost of realizing hard and resistant industrial goods is utilization of only a thin carbide layer on the surface. A widely used technology for this is thermal cementing of the tungsten carbide powder (with a metal binder) on the surface of metals of a lower melting point. An alternative method is thin film synthesis by physical vapor deposition (PVD), such as magnetron sputtering or vacuum arc. Utilization of an arc discharge allows generation of more intensive material flux and, consequently a higher deposition rate compared to magnetron sputtering. However, an inherent property of arc is generation of so called macroparticles (also called droplets), which may be undesirable due to the possible influence on the structural quality and the surface roughness of the deposited films.¹ There are to date no reports focused on macroparticle generation from a WC cathode used in a DC arc discharge, which is the scope of the present work.

It is generally accepted that macroparticles are a result of the explosive nature of the arc spot and caused by the presence of a pool of liquid cathode material and a time-varying pressure of the plasma exerted on that spot.² In studies on elemental cathodes, an increased abundance of macroparticles have been reported for lower melting point materials when comparing Cu and Cd,³ Ti and Al,⁴ as well as considering a range of metals (W, Pt, Ni, Cu, Ag, Pd).⁵ Recently, also a new mechanism for macroparticle generation from a compound cathode was suggested,⁶ based on thermal effects from the arc spot on the cathode surface, where a discrepancy in melting/evaporation points of the elements in a compound cathode can lead to explosive-like evaporation of one of the elements and generation of supersize droplets. More details can be found in Ref. 6. Moreover, generation of two types of droplets with

distinct differences have been observed when arcing from an $\text{Al}_{0.7}\text{Cr}_{0.3}$ compound cathode in an O_2 atmosphere.⁷

In the present work, we show that even for a relatively high decomposition/melting point material such as tungsten carbide (~ 3100 K), arcing is accompanied by intensive generation of macroparticles. Through visual observation of the cathode surface during and after arcing, and by close examination of the generated macroparticles, a new mechanism for macroparticle generation is suggested. The mechanism is based on the so called Leidenfrost effect at the cathode surface and the explosion of the contact area between a droplet and the cathode body.

2. EXPERIMENTAL DETAILS

The experiments were performed in a cylindrical deposition system of an inner diameter of 700 mm equipped with an industrial scale DC arc source with 63 mm diameter cathodes, including no separate anode. Figure 1 schematically shows the used experimental setup.

Figure 1. Schematic representation of the experimental setup (top view).

A WC ($\text{W}_{0.50}\text{C}_{0.50}$) cathode with a purity of 99,9 wt% was used as produced without any binder by powder metallurgy, with a grain size of the WC powder up to $5\ \mu\text{m}$, see Fig. 2 (a).

Figure 2 (b) shows that the surface of the as-made cathode is relatively smooth. The arc current used in all experiments was 70 A, and the base pressure was $\sim 5 \times 10^{-6}$ Torr ($\sim 10^{-4}$ Pa). The discharge voltage was 17-19 V. No external magnetic field was used. Microscopy diagnostics were performed by using a LEO 1550 scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

Visual observation of the arc discharge from a WC cathode shows generation of a very large amount of glowing macroparticles. Figure 2 (c) demonstrates a photo of the WC cathode surface during operation, taken through a glass window by a digital camera Nikon D800⁸ (Objective Nikkor 50/1.8; the aperture 8; sensitivity ISO 100) with an exposure time 1/150 sec (~ 7 ms).

Figure 2. SEM pictures of (a) the WC powder used to make the cathode, (b) the grinded surface of the virgin cathode, and (c) macroparticle flux from the WC cathode at a base pressure of $5 \cdot 10^{-6}$ Torr.

Initially, the intention was to study the macroparticles by SEM diagnostics of a substrate placed ~ 33 cm from the cathode. However, the substrate surface was found smooth with

incorporation of only a few small ($< 1\ \mu\text{m}$) droplets, see Fig. 3 (a). This may be due to scattering upon impact with the substrate surface, which suggests that most of the droplets in the observed flux are solid during their flight, or at least upon impact with the substrate. Solid droplets have a higher probability for being reflected² which can hamper droplet incorporation. Altogether, the intensive flux of visible macroparticles suggests a number and geometrical size large enough to allow them to be collected from the bottom of the deposition system. For this purpose, a special metallic cup (diameter $\sim 50\ \text{cm}$; height of the walls $\sim 7\text{cm}$) was placed inside the vacuum chamber. Macroparticles of a total volume up to $4\ \text{mm}^3$ were collected after 15 minutes of arc operation. Most of the collected macroparticles were found spherical with a diameter in the range from $20\ \mu\text{m}$ up to $35\ \mu\text{m}$, as exemplified in Figure 3 (b), showing SEM diagnostics of collected droplets. The random orientation of the droplets during analysis prevents examination of the complete surface of every droplet. However, SEM diagnostics performed on a large amount of droplets (> 1000) motivates the assumption that the vast majority has holes with a diameter of around $4\ \mu\text{m}$ and a depth of about $1\text{-}2\ \mu\text{m}$ (based on droplet cross section analysis) on their surface. Figure 3 (c) shows that the holes seem to be epicenters of a splash.

Figure 3. SEM images of (a) surface of the deposited film, (b) collected macroparticles and (c) of a particle displaying a hole in the center of a splash.

Figure 4 (a) demonstrates that the extensive macroparticle generation gives footprints on the cathode surface. First to note is the presence of spherical formations after arcing of the surface, see SEM pictures of the as-made (Fig. 2 (b)) and the arced (Fig. 4 (a)) surface of the cathode. The size of the protrusions are much larger than the size of the powder used for cathode synthesis, see Fig. 2 (a), and comparable in size with the diameter of the collected macroparticles, see Fig. 3. It was also discovered that two types of craters of different size could be detected on the cathode surface. The first type of crater has a diameter of around 1-2 μm, while the second type, shown in Fig. 4 (b), is characterized by a diameter comparable to the droplets size ~ 30 μm. Moreover, some of the spherical formations on the cathode surface are found to be smooth, see Fig. 4 (c), while the rest of them are found to be eroded and covered by the small craters (1-2 μm). This shows that occasionally arc spots may run also on the protrusions.

Figure 4. SEM images of (a) the eroded cathode surface, (b) of the remains of a splash (crater), (c) a spherical smooth protrusion at the surface, and (d) a corresponding spherical eroded protrusion.

The similarity between the collected droplets and the spherical formations at the cathode surface strongly suggests that these objects are linked. A plausible explanation is that macroparticles are reflected from the system walls and returned to the cathode surface. However, visual observation of the system chamber during arcing shows that returning particles are very rare and cannot serve as an explanation the observed phenomenon.

Another possible link between collected macroparticles and the spherical formations on the cathode surface is that the latter are droplets which were created but not yet accelerated (unborn droplets). The fact that some of the droplets remain at the cathode surface clearly shows that their formation is not always accompanied by acceleration. It should be noted that the cathode surface is vertically oriented in the deposition system, hence gravity is not expected to influence the here presented observations.

It is known, that during vacuum evaporation WC loses mainly carbon with a resulting transformation into a two-phase region ($W + WC$) or ($W_2C + WC$) depending on the evaporation temperature.^{9, 10, 11} Moreover, the WC melts incongruently¹² and at the melting temperature (~ 3100 K), the vapor pressure of carbon above the carbide is ~ 15 Pa.¹⁰ In turn, of all pure metals, tungsten has the lowest vapor pressure. For example, at 3000 K, the vapor pressure above tungsten is only 0.01 Pa.¹³ The discrepancy in the vapor pressures suggests that in the area around the arc spot where the surface is in the liquid phase, there is very likely intensive generation of C vapor. The generation of carbon vapor is expected to occur in all directions from the surface of the molten volume, even from the surface facing the cathode body. This can create the conditions needed for the Leidenfrost effect (the “dance” of water droplets on a hot griddle) with a resulting formation of the melt into a sphere. Phase composition of collected droplets based on X-ray diffraction analysis (not shown here) indicates presence of WC as well as W_2C , though more pronounced peaks for W_2C , which supports loss of carbon in connection to droplet generation. Wetting effects with a contact angle between the melt and the solid cathode body may also contribute to the sphere formation.

We have observed that generation of visible macroparticles from a new WC cathode is initiated already after a few seconds. This is consequently the time required for establishing the conditions needed for possible formation and removal of spheres droplets (spheres) from the surface. With elapsed time of arcing, the number of spherical protrusions on the WC cathode is increased as well as the probability of arc spots running on these formations. The critical point of such event is the reduced contact area between the sphere and the cathode body. From the theory of wire explosions, it is known that for a critical current density, the conductor will explode.¹⁴

In Fig. 5, the schematic stages of the here proposed macroparticle generation and acceleration mechanism is presented. Stage 1 – the arc spot melts a small volume of the cathode surface. Stage 2 and 3 – the molten volume starts taking the form of a sphere due to loss of carbon through evaporation (Leidenfrost effect), with a resulting reduced contact area. Stage 4 – Joule heating followed by explosion at the contact, and a resulting acceleration of the droplet. Since the arc spot is non-stationary, the explosion can occur in connection to the formation of the sphere, if the arc spot is then still at the sphere, or at a later stage upon the return of the arc.

Figure 5 Schematic representation of the stages of the here proposed macroparticle generation mechanism, based on the explosion of the contact area between the sphere and the cathode surface.

Figure 2 (c) and all visual observations made of the material flux during arcing show that the vast majority of the droplets have a direction which is not perpendicular to the cathode surface. This can be explained by the force on the particle resulting from a combination of a backward pressure from the arc spot on the sphere, and the pressure from the exploding contact area. Due to the unpredictable location of the arc spot on the droplet in time of the

contact explosion, the direction of the droplet acceleration indicated in Fig. 5 (d) should be considered only as a simplified schematic.

The geometry of the cathode-droplet contact at the time of the explosion and corresponding electrical current density can be estimated as follows. The collected W-C macroparticles have diameters around 30 μm . Assuming that the porosity of the droplets is insignificant and that the density is in the range $15 \times 10^6 \text{ g/m}^3 - 17 \times 10^6 \text{ g/m}^3$ (density of WC and W_2C respectively), then the mass of a droplet m_m is approximately 0.24 μg . The droplet velocity v_m can be roughly estimated by comparing the path length of the macroparticles in Fig. 2 (c) and the diameter of the cathode (63 mm), indicating that the trajectories are in a range of 5 mm – 150 mm for an exposure time of 7 ms. A more precise estimation of the trajectories is not realistic due to different path directions of the droplets relative to the camera. As a result, the estimated velocity of the macroparticles in the photo is in the range 5 – 20 m/s. At the same time, the explosion at the contact area implies that a limited volume of material of a mass m_{exp} will take part in the explosion and attain a velocity v_{exp} . From the momentum conservation law and an assumption that the droplet acceleration occurs due to impact with the exploded mass, we can estimate the droplet momentum and the momentum of exploded mass to be roughly equal. This can be written as

$$m_{exp} = \frac{v_m}{v_{exp}} m_m \quad (1)$$

The explosion velocity v_{exp} can be approximated with the average velocity of anomalous ions from the arc spot, as suggested by Mesyats in Ref. 15. For a W cathode, the average ion velocity is around 11 km/s.² Assuming that the macroparticle mass is 0.24 μg and its velocity v_m is 15 m/s (see calculation above), then expression (1) gives an exploding mass m_{exp} equal to $3.2 \times 10^{-4} \mu\text{g}$.

With a depth of the droplet holes of 1 μm - 2 μm (Fig. 3 (c)), the geometry of the exploding volume can be found by representing the contact volume with a cylinder of a height

of 2 μm . The diameter of the cylinder is obtained from the material density and the above calculated exploding mass, and is found to be equal to $\sim 3 \mu\text{m}$, with a contact area of $\sim 7 \times 10^{-12} \text{ m}^2$. An arc current of 70 A through that area gives an electrical current density of $\sim 9 \times 10^{12} \text{ A/m}^2$, which is comparable to values previously reported where theory of wire explosions has been used to explain the nature of the arc spot.^{15, 16, 17, 18} Furthermore, the calculated diameter of the exploding contact area is comparable with the typical size of the holes observed at the droplet surfaces, see Fig. 3 (c). Considering that not all exploded material promote acceleration of the droplet, the calculations performed above are a rough estimate. Still, they support the assumption that holes and the remains of a splash (Fig. 3 (c)) at the surface of the droplets are footprints of the droplet acceleration process. The formation of holes at the droplet surface seems to occur in line with the electrical discharge machining (EDM) process, which is based on hole formation by high density electrical current.^{19, 20} The large-size craters at the cathode surface (Fig. 4 (b)) is also very likely a footprint of the droplet acceleration mechanism.

The present study is of importance for further understanding of macroparticle generation in DC arc plasma processes, with an aim to increase the process control and potentially provide paths for tuning, or even mitigating, macroparticle generation. This is crucial for controlled materials synthesis, however, process control also provides potential for use of macroparticles in chemical and catalytic industries, where particle size and hence reactive surface area, is the key parameter for optimal functionality. Moreover, this work shows the importance of detailed analysis of the cathode surface as well as the generated macroparticles for further understanding of the non-stationary surface explosions in a DC vacuum arc discharge.

CONCLUSION

In conclusion, we show that arcing from a tungsten carbide cathode is accompanied by an intensive generation of visible macroparticles of a size in the range of 20-35 μm , despite a relatively high decomposition/melting point of the material ($\sim 3100\text{ K}$). A mechanism of macroparticle generation is suggested based on incongruent melting of the WC, which causes intensive sublimation of C from the liquid cathode material associated with the arc spot, with formation of a spherical droplet through a mechanism similar to the Leidenfrost effect. An explosion initiated by a Joule heating through a critical contact area between the droplet and the cathode body is suggested to be responsible for droplet acceleration.

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Figure captions

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