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Process development for stabilization of vacuum arc plasma generation from a TiB$_2$ cathode

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ABSTRACT
Herein, we present stable and reproducible arc plasma generation from a TiB$_2$ cathode. The process development contains three complimentary features: Use of a Mo cylinder around the TiB$_2$ cathode improves arc ignition and stabilizes the process by keeping the arc spot at the cathode surface. The evolution of the cathode surface during erosion and the process stability is further improved by addition of 1wt% carbon in the cathode, with no resulting change in plasma characteristics (ion energy, ion charge states, macroparticles). Finally, an increased plasma density through use of a separate anode provides the last key point, which together with the other two contributes to highly controlled plasma generation from TiB$_2$ using DC vacuum arc, and complete utilization of the cathode material. The combined results provide a novel and efficient route for synthesis of metal borides.

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I. INTRODUCTION

Physical vapor deposition (PVD) is a commonly used method for producing e.g. wear resistant, protective and decorative coatings. PVD is based on the process of transforming the material to be deposited from a solid phase, to a vapor (plasma) phase, with subsequent condensation in the form of a thin film. For industrial PVD, DC arc evaporation is one of the most commonly used techniques for synthesis of hard coatings, mainly due to its ability to operate with any conductive material, including refractory ones, and with a relatively high deposition rate. However, to date, metal borides, with applicable properties such as high melting point, high hardness, and good thermal and chemical stability, are not synthesized from industrial processes based on the DC arc technique. In particular, TiB$_2$ is a stable, super hard and electrically conductive material with a high melting point. These properties are important for hard and protective coatings, potentially improving tool performance in abrasive, corrosive and high temperature environments. However, there is no reproducible synthesis of TiB$_2$ from DC arc evaporation. From the reported few attempts on use of TiB$_2$ cathodes for thin film synthesis by arc, extensive instability caused by destruction of the cathode can be concluded. An explanation thereof is found in large temperature gradients within the cathode during arc processing and the thermal expansion coefficient of the boride. Routes for improving the process stability, such as addition of carbon, applying a “suitable” magnetic field, using pulsed arc, or working in a reactive atmosphere, have already been suggested. However, these routes remain to be confirmed or further developed.

In Ref. 7, we showed stabilization of plasma generation from a TiB$_2$ cathode by modification of the magnetic field used in the arc source. It was discovered that in the absence of any external magnetic field, the crystalline structure of the TiB$_2$ cathode with protruding crystal edges leads to arc spot dissipation. The dissipation results in a reduced current per spot and hence a larger area subject to heating by the arc current. The latter allows a reduction of local heating on the cathode surface and a more stabilized DC vacuum arc. Moreover, an increased probability of ignition of new spots
ments, the arc source was operated at 70 Amps arc current (Ionbond) with cathodes of 63 mm in diameter. In all experiments, the arc source was operated at 70 Amps arc current at a system base pressure around $10^{-6}$ Torr. The cathodes were provided by PLANSEE Composite Materials.

II. EXPERIMENTAL DETAILS

The experiments were performed using a deposition system equipped with an industrial scale DC arc plasma source (Ionbond) with cathodes of 63 mm in diameter. In all experiments, the arc source was operated at 70 Amps arc current at a system base pressure around $10^{-4}$ Pa ($\sim 10^{-6}$ Torr). The cathodes were provided by PLANSEE Composite Materials.

A permanent ring magnet, which usually serves to keep the arc spot on the working surface of the cathode, is excluded from the source scheme. As commonly used in industrial scale DC arc plasma systems, the walls of the grounded vacuum chamber play the role of the anode in the setup, see Fig. 1.

III. RESULTS AND DISCUSSION

To investigate routes for control of the arc movement on the cathode surface, it has to be noted, that the arc spot itself does not move. Instead, a track left by the arc discharge is a path showing the propagation of consecutive explosions. A new arc spot is ignited when there is a point at the surface close to the already operating spot where the electric field strength increases above a critical level, leading to a drastic increase in emission of electrons, and a micro explosion in the form of a new arc spot. This spot is electrically in parallel to the one already in operation. Due to a hot cathode zone and liquid phase formation, the new spot will have a lower total resistance and therefore provide favorable conditions compared to the parent spot. It will take over the current from the original spot, and as a result accelerate the cool-down of the parent spot, a process through which the arc spot looks shifted. Based on this, the formation of a new spot occurs at a surface point which is able to provide favorable conditions for spot generation through, e.g., a lower critical electric field strength, which in turn is determined by the surface material. Consequently, if the spot glows at a border of two different materials and there is a symmetrical spatial distribution of the plasma density around that spot, as expected in the absence of an external magnetic field, the arc will preferentially move to the material with the lowest critical field strength for arc ignition. The electrical potential of the discharge, also called the burning voltage, is directly correlated to the critical electric field strength. Therefore, the arc spot will have a preference for glowing on a material based on the discharge potential. This can also be understood by considering that the arc discharge strives for the lowest cost of power. Therefore, the material which is able to provide a lower total power (potential multiplied with arc current), is the one preferred in the arc process. Based on the above, and with an aim to keep the arc spot on operational surface of the TiB$_2$ cathode, we suggested to surround the cathode by a material which has a higher discharge potential.

In the here preformed experiments, the potential of the arc discharge with a TiB$_2$ cathode used at base pressure is $\sim 25$ V. An example of a material providing a higher discharge potential for the same conditions is molybdenum, $\sim 30$ V. Hence, use of Mo at the outer border of the TiB$_2$ cathode is suggested for retaining the spot movement to the TiB$_2$ surface. Figure 2a shows a schematic of the proposed cathode assembly for a standard 63 mm cathode. The outer diameter of the Mo cylinder is 63 mm, with wall thickness of 3 mm. The cylinder and the cathode are electrically connected, with a maximum distance in any point being below 0.3 mm.

The schematic picture also shows the arc ignition system, commonly used in industrial scale DC arc plasma sources.
FIG. 2. a) Schematic of cathode assembly with a Mo cylinder around the TiB$_2$ cathode. Operational surface of TiB$_2$ cathode after 20 min of operation b) without and c) with the Mo cylinder.

The arc is ignited by a short strike of the trigger pin, driven by a pneumatic system. The trigger pin is adjustable concerning the distance to the cathode, to compensate for cathode erosion during the arc process. During ignition, the current going through the trigger to the contact area, igniting the arc, leads to high temperature gradients. It can therefore be expected that this area may be subject to higher thermally induced stress, etc., compared to the rest of the cathode surface. This issue is resolved by the Mo cylinder, as the arc can be ignited by a touch of the pin on the cylinder. As the arc preferentially glows on TiB$_2$, the spot is transferred to the operational cathode surface. Fig. 2(b–c) shows the TiB$_2$ surface after arcing without and with the cylinder, respectively. Please note, that the cathode in Fig. 2(b) has been rotated clockwise after being in operation and before taking the photo. Evidently, the cathode is more intact when a cylinder has been used. Furthermore, erosion of the cylinder is insignificant, confirming the assumption of preferential arcing on the boride. Visual observations during the experiment also showed that the arc glows preferentially in the central part of the cathode.

An additional route for increasing the process stability and for preventing cathode destruction is to hamper the propagation of the cracks. For that purpose, a small amount of carbon powder is added to the cathode material before sintering. It is claimed in Ref. 11, that the mixing procedure used during preparation of the cathodes leads to carbon particles located around the TiB$_2$ grains, which in turn leads to an improved resistance against thermal fatigue, reduced stress, and reduced crack propagation. In a comparison between arcing from a TiB$_2$ and TiB$_2$ +1wt% C cathode, we have performed plasma diagnostics with a mass-energy-analyzer (MEA, Hiden Analytics model EQP) placed at distance ∼33 cm from the cathode surface, in line with previous work.12 We find that there is no influence of C on discharge characteristics such as plasma composition, ion energies, ion charge states, and intensity of macroparticle generation (not shown here).

Fig. 3a shows a TiB$_2$ cathode used for >30 minutes, to be compared with Fig. 3b, where the beneficial influence of C on the cathode evolution is evident from a reduced amount of cracks, and a more uniform erosion of the cathode surface.

Carbon additions may have an additional role for improving the TiB$_2$ arc process through a possible increase in conductivity of the cathode material, as it has previously been suggested that an electrical resistivity and/or a low density are disadvantageous for arcing from a TiB$_2$ cathode.13

A third route for optimization of the TiB$_2$ arc processing is based on arc dissipation. As discussed in Ref. 7, an increased electric field at the edges of TiB$_2$ crystals at the cathode surface promotes ignition of arc spots. In the absence of an external magnetic field (no spot steering), this can lead to a critical electric field strength being reached at different areas of the cathode surface simultaneously, and consequently lead to operation of more than one arc spot (the spot dissipation phenomenon) and/or an increase in the spot velocity. This stabilizes arcing from a TiB$_2$ cathode by a reduction in the local heat load. However, for the present work, it should be noted that the actual strength of the electric field is determined by the difference between the potentials of the electrodes, and the distance between them. In the DC arc discharge, with a continuous presence of plasma between the electrodes, a major part of the discharge potential is dropped near the cathode, within the cathode potential layer. Therefore, the thickness of that layer determines the field strength. The thickness of the layer, in turn, depends on the plasma density near the cathode. Since a stronger field may contribute to arc
stabilization, methods for variation of the plasma density near the cathode have to be considered, where one such method is to reduce the volume available for the plasma. Industrial arc sources typically have no separate anode, instead the chamber walls play the role of the anode, with a resulting large cathode–anode distance and a wide angular distribution of the generated plasma. To reduce the distance and the angular distribution, it is possible to use a separate anode, which can be made smaller, be of a specific geometry, and placed closer to the cathode compared to the chamber walls. In this case, the plasma will be primarily within the cathode–anode distance and its angular distribution will also be limited by the geometry of the electrode gap.

The influence of a separate anode on the arc stabilization has been studied by positioning a disk anode with a hole for passage of the generated ions (diameter 55 mm) and with a slit for the trigger pin at a distance of ∼2 mm from the cathode assembly, see schematic in Fig. 4a.

![Diagram](image)

**Fig. 4.** a) Complete scheme of the tested source assembly, and (b) a TiB$_2$+1wt% C cathode used for more than 2 hours.

The small distance between the cathode and the anode leads the anode being subject to extensive heating. In this work, a cooling system for the anode has not been considered, though, based on the choice of anode material, it may not be needed. Our first experiments with a stainless steel anode and simultaneously performed plasma diagnostic showed contamination of the ion flux by anode material. Changing the anode material to TiB$_2$, no anode ion contamination was detected, and the plasma composition was approximately the same as that measured when there was no anode. It should be noted that the MEA does not provide data that can separate Ti$^{4+}$ and C$^{+}$ ions, neither distinguish between B and C ions of charge ≥2. Therefore, no estimation of the carbon content in the plasma can be made for use of a TiB$_2$+1wt% C cathode.

Fig. 4(b) shows the surface of the TiB$_2$+1wt% C cathode after arc plasma generation for more than 2 hours using the arc source assembly shown in Fig. 4a). Smooth surface erosion is clearly seen, with no cracks and no detached cathode pieces, compared to the previous images in Fig. 2 and 3. A slight difference in erosion depth over the surface can, however, be noted, which is the topic of future optimization. It should be stressed though, that the here presented process optimization allows complete cathode utilization, with arcing to the point of complete removal of the cathode material, shown in our experiments.

Macroparticle generation is an inherent feature of arc plasma generation. Visual observations from our experiments show an intensive flux of macroparticles. While we have previously shown that incorporation of these particles in the metal boride thin film is very limited, a significant part of the material flux from the cathode is consequently lost during film growth. This loss may be reduced by tuning of the cathode composition and/or change of the cathode structure, potentially changing the mechanism of droplet generation. Further exploration of the conditions of the operational cathode surface, the effects from impurities (compositional and structural) on the cathode behavior, and of adjustment of the discharge gap, will improve the fundamental understanding of arc plasma generation from diboride cathodes, and allow synthesis of new/optimized materials and compositions through control of the arc process.

**IV. CONCLUSION**

In conclusion, we have explored DC arc plasma generation from a TiB$_2$ cathode and have identified three complimentary key features for attaining a stable and reproducible process. First, we show that use of a Mo cylinder around the boride cathode limit the movement of the arc spots to within the rim of the cathode, and also improve ignition of the discharge. Second, an improved process stability and a reduced cathode destruction is obtained with a TiB$_2$ cathode containing 1wt% of carbon, an effect which is even more pronounced by the third route, use of a separate anode. The latter is suggested to lead to increased arc dissipation and an increase in plasma density near the cathode. Altogether, the combined optimization procedures realize a process stability for arcing
of borides superior to previous reports and allow smooth and complete erosion of the cathode material. These results are of importance for the utilization of cathodic arc as an efficient method for synthesis of metal borides.

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