Original Article

The behavior dynamics of a droplet phase in vacuum arc discharge plasma in chemically active gas nitrogen

Valentin Ye. Panarin, Nikolay Ye. Svavil’ny*, Anastasiya I. Khominich
G.V. Kurdyumov Institute for Metal Physics of the National Academy of Sciences of Ukraine, Kyiv, Ukraine

ARTICLE INFO
Article history:
Received 8 December 2016
Accepted 25 April 2017
Available online 9 July 2017

Keywords:
Vacuum
Arc discharge
Cathode surface
Titanium nitride
Microdroplet

ABSTRACT
The charge distribution of microparticles produced at the cathode surface in the vacuum arc discharge under conditions when the reactive gas nitrogen is present in the discharge gap was studied with an electrostatic analyzer. Small fragments of titanium nitride that form on the surface are heated to electrons thermionic emission temperature in the plasma while they drift to the substrate which causes a positive charge, while the large fragments are cold, that is why they are negatively charged. The titanium microdroplets are mainly positively charged, and they keep this charge for a long period and causes difficulties of filtration in plasma streams.

© 2017 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction
Vacuum arc discharges are widely used for deposition of thin films and coatings of solid phase substances on a variety of materials [1,2]. Physical processes occurring in plasma flows that are generated by vacuum arc discharge are the subject of constant interest of researchers [3-5]. The microdroplets phase of the spray material (droplet size from fractions to units and sometimes even tens of microns) is always present in the plasma flows of the steam generators of the cathode material in addition to the ionic and atomic component [6,7]. It is necessary to get rid of the component, and different separators are normally used for this purpose [8]. However, the component is not always undesirable, because it is capable of maintaining and transferring the compound of complex heterophase alloys (eutectic, shape memory alloys, intermetallic compounds), by which the sputtering cathode is produced of [9], on the substrate. Furthermore, vacuum arcs can be used to generate micron sized powders of any electrically conductive materials. Therefore the droplet component of the plasma flows in vacuum arcs often can present very useful fraction of evaporated material.

For these reasons, it is very important to understand the physical processes that occur on the surface of freely flying microparticles in plasma flows generated at the cathode evaporation vacuum arc discharge.

* Corresponding author.
E-mail: svavil@imp.kiev.ua (N.Y. Svavil’ny).
http://dx.doi.org/10.1016/j.jmrt.2017.04.004
2238-7854/© 2017 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
The dynamics of microdroplet phase of cathodes working materials in the operation of the vacuum-arc discharge in an inert argon ambient gas has been studied in earlier publications [10]. The addition of the reactive process gas in the discharge gap substantially changes the conditions and the functioning of the discharge and the physical processes in the discharge gap. The reason for that is the appearance of the reactive gas in the vacuum volume substantially changes the physical processes at the biggest working surface of the cathode. The thin films of chemical compounds of the gas are formed at the cathode, and they enter into a chemical bond with the plasma component of the cathode material that vapors directly onto the surface [11]. This leads to changes in the origin and evolution conditions of the emission cathode spots on the cathode, through which, in fact, vacuum arc operates [12]. Furthermore, in the presence of the droplet phase in plasma flows reactive gas may form a compound on the droplets both as with a droplet of the material and with the ion component streams coming to the droplet surface during its drift in the discharge gap. In this case the working cathode material microdroplets may be coated with one or another functional layer of the chemical compounds of the cathode material with gas component of the discharge – this could be important in finding the solution of the problem of obtaining cathode material nanopowders with special properties.

The results set out below are devoted to the studies of the effectiveness of reactive gas nitrogen on the physical processes in the discharge of the standard [2] technological plasma arc device (PAD).

2. Experimental conditions and discussion of findings

The experiments took place in a vacuum system, schematically represented in Fig. 1, the physical processes were investigated by methods described in detail in [10].

Nitrogen was used as the working gas and collimated deposition system streams on a substrate (6) dismantled together with the flange (7) and the substrate (6) in some experiments. In these cases, the Ø78 mm copper substrate holder was attached to copper foil after the flap (5). The foil served as a substrate for a plasma stream, now freely propagating from the open volume of the discharge gap of the PAD to the volume of the discharge gap of the vacuum chamber. In this case, the flow particles from the cathode were deposited both on the front and on the back parts of the substrate holder and it was possible to apply a bias voltage on either of the signs.

Microdroplets on the surface of the silicon substrate and the copper foil were investigated by a scanning microscope JEOL JSM 6700F.

The experimental studies of the dynamic behavior of microdroplets in the cathode–anode discharge gap and as they drift in the vacuum chamber to a substrate (6) in the presence of nitrogen were carried out at different retarding potentials of the tearing grid analyzer (10). Nitrogen working gas was let in the vacuum chamber to pressures, typically implemented in the synthesis of titanium nitride.

The data presented in Fig. 2 demonstrates that if a large “minus” is on the fracture grid (all the ions and positively
charged microdroplets are free to penetrate the analyzer to the substrate), then the nitride film formed on the substrate is homogeneous – Fig. 2a. But when positive grid is applied on detaining grid (Fig. 2b) – the uncovered titanium film locations are visible on a substrate. The reasons for observation these places are: while applying a positive retarding potential to grid the positive ions are reflected by it and cannot get to the substrate (the overwhelming majority of the deposited particles are ions in vacuum arc discharges) [10]. Which leads the film on the substrate being thin and not covering the seats of heterogeneity. We also see that the substrate coated with a thick homogeneous titanium film (Fig. 2a) has some dark round points-tracks created by microdroplets after hitting the substrate at a temperature of about 600 °C.

The data presented above is a noteworthy important fact – solid pieces of material with a shape that differs from the circle are appeared on both substrates except microdroplets (they were not in the case of argon (see [10])). However, when the negative potentials are on the grid (Fig. 2a), the pieces that are capable to reach the substrate are very small, and they carry whether positive charge on themselves (which is very likely), whether if they are negatively charged, they carry a very high kinetic energy and are able to overcome such a considerable delay. Large pieces are visible only when a positive potential is on the detaining grid – then back again, whether they are negatively charged, and then they are accelerated by this potential (this is most likely), either being charged positively, they also have an incredibly high energy movement. There are no reasons to assume that the large pieces of the cathode material observed on the substrate have a positive charge. As the analysis follows in [10], a positive charge on the microparticle can be occurred exclusively during its heating to the emission temperature. The larger the microparticle, the least likely it would be heated up to this temperature, with all other things being equal. It is obvious that all these fragments are parts of destroyed titanium nitride film formed on the surface of the titanium cathode. With the explosion of emission cathode spots on the cathode [13], covered with the nitride film, solid pieces of nitride are formed in the form of debris and drift to the substrate. They have not turned into a drop during the drift time. (There is a full stream of plasma ions on the cathode surface, as for any negatively charged electrode in the plasma, in this case are titanium ions. Therefore, the nitride film is naturally formed on it as well as on the substrate. Of course, it is very thin, since it continuously demolished from the cathode surface at a discharge operation. We can see how the pieces of the cathode nitride film arrive to the substrate during the functioning of the arc.)

Why do we see so much debris on the substrates in the synthesis of nitride film? After all, when titanium had been sprayed in a neutral gas argon (see [10]) the clear debris were whether completely absent, or there were so few of them on the substrate that they could be misunderstood to be just “dirt”, that is often found on the surface of substrates.

It should be kept in mind that, firstly, titanium nitride has a significantly higher melting temperature (3223 K [14]) compared to titanium (1933 K). Apparently for this reason there is not enough incoming ion energy for many cathode nitride pieces to be overheated during the drift to the substrate and turn into a drop. Secondly, with the appearance of the nitride film on the cathode the evolution of the emission spots on the cathode changes dramatically. At least, the conditions for the emergence of the field emission cathode on the nitride film may be easier (i.e., the process of the primary origin of the spots is easier) because of the great heterogeneity of the phase surface of the titanium cathode at its dynamic covering up with titanium nitride. Therefore, there are more emission spots generally formed in the presence of nitride film than on the pure titanium cathode. Principally, a titanium nitride coating on the cathode cannot grow homogeneous due to the continuous operation of the arc on the surface. This should greatly facilitate of the emergence of new emission centers precisely on many frontiers of phase inhomogeneities [12,13].

Moreover, it is natural to assume that arising on the cathode surface emission centers can reach the melting state much easily on the cathode surface to the melting state is energetically more favorable both under the nitride film or on the border of the existence of the film on the cathode surface. The reason is that the melting temperature of the cathode material (i.e. titanium) is lower than the nitride film that is
located close to it. The emerged microspot evolves under the influence of a dense ion component of the plasma discharge, and explodes as if under the nitride film (or on the border as close as possible to the film). With these many nitride pieces (the melting point of which is significantly higher than titanium) present on the cathode surface, start from the explosion place, apparently having an average, even somewhat lower initial its own temperature than the temperature of super-heated titanium droplets emitted from the liquid titanium microbasin of the emission spot.

Thus it can be explained by a fairly large number of nitride fragments that appear on the substrate at a discharge operation of the titanium cathode chemically active gas nitrogen. These solid pieces of finished titanium nitride (big and small) are very poorly integrated in the surface of the substrate and it is necessary to synthesize the original nitride film on them and thus can be, for example, centers of corrosion in anticorrosion coatings. Most likely, such processes can also occur in the synthesis of aluminum nitride, as well as other composite compounds, when other reactive gases are used for the plasma synthesis.

Attention is drawn to another important fact, manifested in the deposition of the nitride film on a standard substrate, being under negative potential: it turns out that the titanium drop can carry a positive charge for quite a long time.

The confirmation of this conclusion may indicate the results of experiments with the application of thin films of titanium nitride on the back side of the substrate Ø78 mm (in these experiments, instead of the heated substrate (6) mounted cold substrate holder Ø78 mm with copper foil on the reverse side thereof). Fig. 3 shows images of the copper foil surface, reinforced at the backside (toward to the flow of plasma from the PAD) of the substrate. Discharge mode for the standard synthesis of titanium nitride.

It is obvious that titanium drops are present therein (possibly, they are covered after deposition of nitride on the substrate), but there are just a few irregular shaped pieces (fragments) of the solid substance. If the observed drips and fragments do not carry a charge (i.e. they will be neutral), they would have no chance to get on the opposite side of the substrate. Neither direct interaction collision mechanisms of very heavy (compared with atoms, ions) microdroplet with atoms (ions) of the working gas in the chamber could change the trajectory of any neutral microdroplet (which flies frontally to the surface of the substrate) to 180°. Furthermore, since there was a significant (−60 V) retaining potential for negatively charged droplets on the substrate, the only possibility for a drop to get on a substrate in the backside – is to carry a positive charge on itself.

Indeed, if the drop is positively charged, it will drift like any ion after the highly mobile electrons occupy any free plasma space behind the large size of the substrate (i.e., a drop will be tightened to the substrate together with positively charged ions, self-consistent electric field arising in the diffusive plasma because of the more mobile electrons). Upon reaching the substrate, the positively charged drop will be accelerated in a layer near the substrate to an energy determined by the application to the substrate of a negative potential.

Probably, the reason for nonspherical titanium nitride pieces (fragments) not being visible on the backside of the substrate is that the temperature of the electron emission of these pieces is higher than the emission temperature of pure titanium droplets. And therefore the pieces do not carry a positive charge (more about this in [10]). Anyway, it is obvious that there is not enough energy brought by the ions flowing to the surfaces of the solid pieces. Thermionic emission (when all fragments reach thermionic emission temperature) does not compensate the plasma electrons flow to them. Hence, the ionic component arriving during fragments drift in the discharge gap at their surface, in principle, are not able to charge them positively during the drifting to the backside of the substrate. Either they are charged negatively or their charge is close to zero and the effect of electric fields on the particles is minimal.

And the presence of the positive charge on the microdroplets of pure titanium greatly complicates their filtering of positively charged ions, which just needs to be preserved as much as possible in the process of filtering plasma flows and bring positive particle ions to the substrate.

3. Conclusions

The operation of the vacuum arc discharge with cathode spot in reactive gases formed compounds on the cathode surface. They can be transferred onto the substrate in forms of pieces of solid phase in the final synthesized form. Fragments of such compounds have a high melting point, so they retained for a long time in the solid phase and poorly integrated into the deposited film. These fragments, as well as microdroplets, in general had worsen the process of obtaining high-quality thin films synthesized on a substrate.

A positive charge was formed on microparticles when they achieved the emission temperature, due to energy of the ions arriving on free flying microdroplets [10]. This charge can be
maintained on them for a long period so they are effectively retained in the plasma flows along with the positively charged ion component deposited on the substrate.

Thereat the separation of positively charged ions from the microdroplets can be done by creating special conditions for a complete evaporation of droplets toward the substrate, or it would be necessary to ensure their cooling at a relative way. The cooled microparticles (i.e. with a temperature below thermionic) do not carry a positive charge and there can be a standard method of separation of repulsive negative bias applied to the substrate in a conventional plasma technology. It is also possible to get rid of positively charged microparticles using low charge to mass ratio such particles, as compared with the ions special separators, in special separators (for example, to direct of the plasma flows to the substrate across the magnetic field [2]). Nevertheless, that is a different technical task.

**Conflicts of interest**

The authors declare no conflicts of interest.

**References**