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Optical emission spectroscopy diagnostics of a Ni Thermionic Vacuum Arc (TVA) plasma

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Thermionic Vacuum Arc is a technology used especially for metallic thin film deposition. In TVA, the high-density plasma is localized above the anode, whereas the substrates are placed away from the core of the plasma. This enables deposition to be carried out at low substrate temperatures even for the highest melting point materials. Although it is arc plasma, the TVA can be used to prepare particle free films of pure materials. The TVA plasma parameters were evaluated using the analysis of the optical emission radiation of plasma. The plasma parameters obtained are anode (Ni pool) temperature, vapour pressure, evaporation rate and electron temperature as function of the dissipated power between electrodes. It was found that plasma parameters are increasing with the power and during arc plasma have relatively constant values.

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Keywords: Thermionic Vacuum Arc, Optical emission spectroscopy

1. Introduction

The film deposition process by thermionic vacuum arc (TVA), a new discharge type in pure metal vapour plasma, might become one of the most suitable technologies to significantly improve the quality of the surfaces coated with different materials using present technologies. The thermionic vacuum arc can be ignited in vacuum (or ultrahigh vacuum) between a heated cathode surrounded by an electron focusing Wehnelt cylinder and an anode (tungsten crucible) containing the material to be deposited. Due to the electron bombardment of the anode by the accelerated thermo-electrons from the grounded cathode towards the anode (which is at high voltage), anode material first melts and afterwards starts to evaporate ensuring a steady state concentration of the evaporated atoms in the cathode – anode space. At further increase of the applied high voltage, a bright discharge is established inside of the deposition chamber (pressure $\leq 10^{-3}$Pa) in the vapours (partial pressure ≈ 133 Pa) of the anode material.

Using this technology we prepared high temperature resistant coatings in order to protect representative devices, as wind holes and the top of lances in iron work industry in order to increase their lifetime. Because these devices are made of high purity copper, refractory metals such as Ni, Cr, Re, W, Mo are promising candidates for improving high temperature resistance due to the high melting points.

2. Experimental set-up

The experimental set-up is presented elsewhere [1] only a brief introduction is given here. A tungsten filament cathode externally heated by a low voltage from high current electrical source, is emitting thermal electrons that are focused by a cylinder Wehnelt on the Ni anode. The Ni anode is placed in a Carbon crucible (see Fig.1).

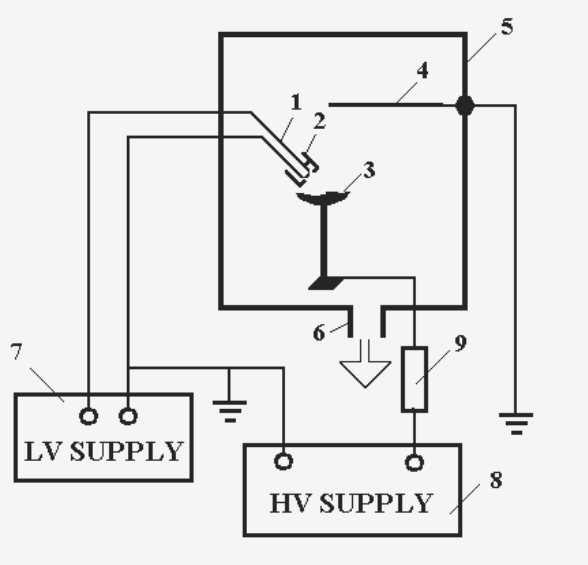

Fig. 1. TVA arrangement: 1-filament, 2-Wehnelt cylinder, 3-graphite crucible filled with Ni pebble, 4-substrate, 5-chamber wall, 6-exhaust flange, 7-low voltage supply for filament heating, 8-high voltage supply for sustain TVA plasma, 9 – balast resistor.

Due to the electron bombardment the anode material can evaporate and when the evaporated atoms become high enough, the electron-atom ionizing collisions can generate the plasma in pure anode material. The

deposition substrate was placed at about 25 cm above the anode. The substrates used for deposition were silicon and glass.

OES analysis was performed using an SM-240 CCD Optical Multichannel Analyser from Spectral Products, USA. The light of the plasma together with the thermal radiation of filament is focused by a convergent lens on the entrance slit of spectrograph.

3. Results

The volt-ampere characteristics of a Ni TVA is shown in Fig. 2 for two filament currents. The breakdown voltage for plasma ignition in pure Ni vapours depends on the chosen values of the filament currents. For the case of 56 A, the breakdown voltage was about 6.5 kV, the stable discharge being established at 2.7-3 A. When the filament current was 60 A, the breakdown voltage was lower (about 5 kV), due to the higher local Ni vapour pressure.

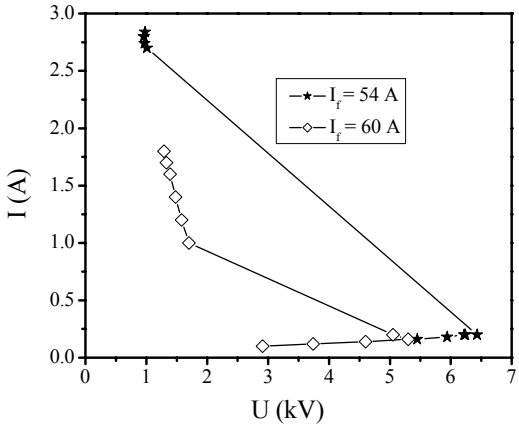

Fig. 2. The volt-ampere characteristics of the TVA plasma running in Ni vapours for two filament currents.

The emission spectrum of the Ni TVA plasma together with thermal radiation emitted by the filament was imaged on the CCD by a lens and a 3 mm iris diaphragm. Taking into account the calibration of the system and using the Stefan-Boltzmann relation, the temperature of the Ni pool on the top of anode was obtained. The emissivity coefficient of the Ni is 0.4. The relative error measurements of temperature Ni surface were estimated to be 10%. An important error source in the estimation of the Ni pool temperature is Ni film deposition on the window, especially during arc plasma running. The temperature of the Ni pool was found at 1500-2500K (melting point of Ni: 1728K). A plot of Ni pool temperature just before ignition and during arc running is shown in Fig.3. A quasi constant temperature behaviour during arc ignition could be seen this figure.

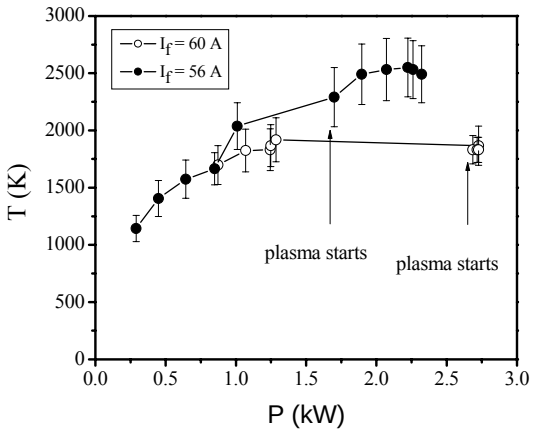

Fig. 3. Temperature of the Ni pool obtained for two filament currents as a function of discharge power.

An important parameter of the plasma is the evaporation rate. The evaporation point enables estimation of the vapour pressure P_v and subsequently of the evaporation rate W, using Clausius-Clapeyron relation [2], by equations (1) and (2).

$$\log P_v = A - B/T \tag{1}$$

$$W = 0.0583 \cdot P_v \cdot \left(\frac{M}{T}\right)^{1/2} \tag{2}$$

where, A and B are given constants [2], depending on the material nature and M and T are the mass and measured temperature of Ni.

The local pressure of the Ni vapours was found around 0.8-1 torr corresponding to a temperature around the Ni melting temperature.

The vapour pressure presented in Fig. 4 was obtained from relation (1).

It was found that the anode temperature increased proportionally with increasing arc current until the moment of plasma ignition, at around 1800 K. As the melting temperature of Ni is 1728 K, it can be concluded that the vapour pressure at this temperature is not high enough for plasma ignition.

The vapour pressure necessary to ignite the plasma for high current of 60A is around 10-40 torr while for a low value current of 56A is necessary vapour pressure of 0.3 torr. If one desire to have a high evaporation rate is better to work with high filament currents, in this case another advantage being low voltage of the arc discharge.

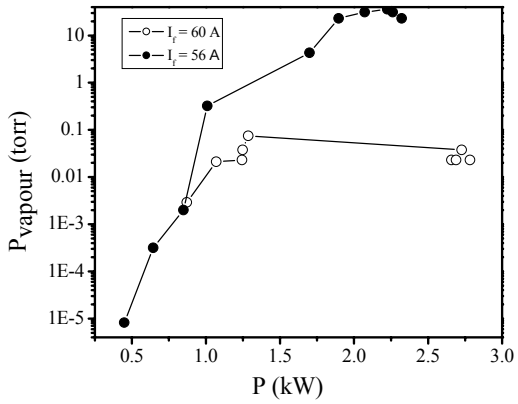

Fig. 4. The vapour pressure before and during arc ignition as a function of the discharge power.

Another important parameter of TVA plasma is the evaporation rate that was calculated by relation 2.

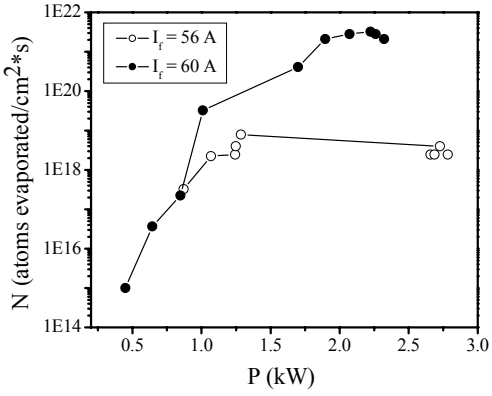

Fig. 5. The evaporation rate of Ni pool obtained for two filament currents as a function of power discharge.

While all anode material is melted in a crucible before TVA plasma ignition for the great majority of known metals, refractory metals like Ni have a different behaviour. The TVA plasma can be ignited in Ni vapours without using a crucible. This is because, apart from the fact that nickel has a relatively high melting point, it also has a very poor heat conduction coefficient. Thus, Ni can only be melted locally, at the point of electron incidence on the anode. Therefore, a Ni rod can be used as anode, instead of the crucible as in the case of all non-refractory metals.

Fig. 6 shows the appearance of the Ni plasma, the substrates (Si, glass, ceramics, and stainless steel) and the gauge of the evaporation speed monitor. A typical optical emission spectrum of the Ni plasma and the identification of the observed lines in the range of 330 to 400 nm are shown in Fig.7. Only Ni I emission lines were observed proving the purity of the produced plasma. The spectrum was taken at 10 mm above the anode (Ni pool).

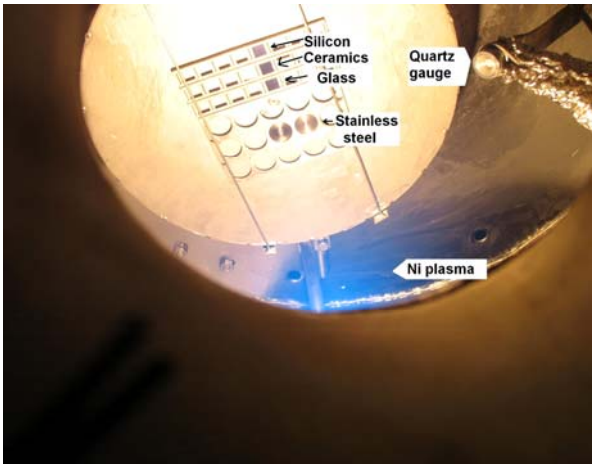

Fig. 6. Photograph of the Ni plasma during Ni layer deposition on (Si, glass, ceramics, stainless steel).

The electron temperature of TVA plasma running in pure Ni vapours was estimated using the method based on the ratio of the emission lines [3] measured using an optical SM 240M spectrometer. The resolution of the spectrometer is around 2nm. The advantage of this technique consists in being an inexpensive and convenient method of characterizing a discharge. Qualitative overview of plasma composition was obtained quickly from the emission lines intensities observed in certain conditions.

As is well known, the intensity of the spectral lines emitted by the plasma depends on the concentration of the emitters and the plasma temperature.

At a sufficiently high discharge current, after the arc discharge has developed fully, the plasma attains the local thermodynamic equilibrium (LTE). In this state, for atoms or ions of the same kind, the relative intensities of the spectral lines emitted by the plasma depend only on the plasma electron temperature [3, 4].

In order to avoid energy calibration versus wavelength and to make the measurements less influenced by plasma fluctuations, the two lines are selected to record on the same target and therefore, the wavelength difference of the two lines must not exceed 90 nm. In addition, another criterion that must be taken into account in choosing the two spectral lines is that the optical transition must take place onto the same energy level.

On the nickel plasma spectrum there are three lines that are more distinctive than others, as one can easily see in Fig.7.

These three lines, whose wavelengths are 380.714 nm, 385.830 nm and 397.356 nm, correspond to transition onto the same level (0.4227783 eV). The spectroscopic data of the three lines were collected from Ref. [5]

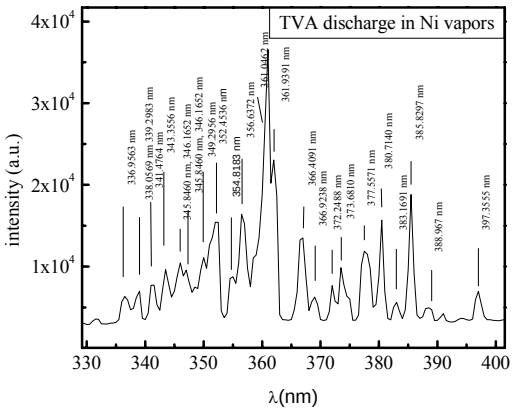

Fig. 7. Typical emission spectrum of the Ni TVA plasma.

Table 1. Spectral data used in this study.

λ (nm)	A_{ki} * 10^{-6} (s^{-1})	E_k (eV)	E_i (eV)	g_i	g_k
380.714	4.3e+06	0.4227783	3.6784768	5	7
385.830	6.9e+06	0.4227783	3.6353109	5	7
397.356	3.8e+05	0.4227783	3.5421295	5	5

T_e of nickel TVA plasma estimated using ratio of Ni I 380.714 nm and Ni I 385.830 nm, Ni I 380.714 nm and Ni I 397.356 nm lines, was found in the range of 2eV, corresponding with other evaluations of metallic plasmas running in pure Cu vapours [4, 6]. The electronic temperature obtained by this method is mentioned as *excitation temperature* corresponding to the high excited states of atoms. Usually such excitation temperature is higher than the electron temperature. The precision of the measured electron (excitation) temperature in the present work is around 0.5 eV.

4. Conclusion

With the plasma parameters: anode (Ni pool) temperature, vapour pressure, evaporation rate and electron temperature a real time control of the Ni thin layer at desired conditions could be done. It was found that plasma parameters are increasing with the power and during arc plasma have relatively constant values. Therefore having the vapour pressure, the evaporation and the deposition rate in real time an optimization of all process parameters could be done.

Acknowledgment

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