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INFLUENCE OF Re ON THE THERMO-ELECTRON EMISSION FROM THORIATED W CATHODE DURING Re DEPOSITION BY THERMIONIC VACUUM ARC (TVA) METHOD

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Since Re deposition was found to be very difficult because of its high melting and boiling points, low vapor pressure and high work function, influence of Re on the thermo-electron emission during Re deposition by TVA method was studied experimentally and theoretically. The problems were successfully solved to obtain uniform Re coatings at a deposition rate of more than 6 μm/h.

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1. Introduction

Ni-base super alloys have been widely used as turbine blade materials but little improvement is expected further more because of their low melting temperature of about 1630 K. Among several candidates for replacing the super alloys refractory metals such as W, Mo, Ta and Nb are expected to be promising ones. Nb alloy has been actually developed for this purpose [1], but its fatal defect is low resistance against high temperature oxidation. This problem, however, can be solved by forming thermal barrier coatings with high resistance against oxidation. Since the coatings must accomplish several kinds of properties at the same time, they are usually multiple-layered, for example, consisting of a stress-relaxation layer to attain high adhesion with the substrate, a barrier against coming and outgoing elements, a reservoir supplying lost elements and a heat resistant layer. For example, Re-Cr-Ni alloys have been proposed for the barrier layer of the Nb alloy [2]. It is very difficult, however, to deposit Re because of its high melting and boiling points, low vapor pressure and high work function.

Re deposition by thermionic vacuum arc (TVA) method [3] was considered as a first step toward obtaining Re-Cr-Ni coatings [4]. The problems of Re deposition are investigated with special interest in thermo-electron emission behavior and their solutions are shown.

2. Experimental set-up and method

The experimental set-up is shown in Fig. 1, where the distinctive feature is the usage of a Re rod. This comes from the fact that no appropriate crucible has been found for Re. For example, when a graphite crucible was used, C was found to be included in the deposited Re film because the vapor pressure of C (40 Pa) is much higher than that of Re (3 Pa).

The Re rod of 8-10 mm in diameter and 60 mm in length was laid on a Mo cylinder, which was rotated by an electrical motor. In order to impede the heat loss by thermal conduction through

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the anode support as much as possible, this was made of a thin W rod (1.5 mm in diameter) supported by a ceramic tube used to insulate the anode from the grounded cathode. A high voltage power supply (0-6 KV, 0-5A) was used to accelerate the electron flux produced by the TVA gun.

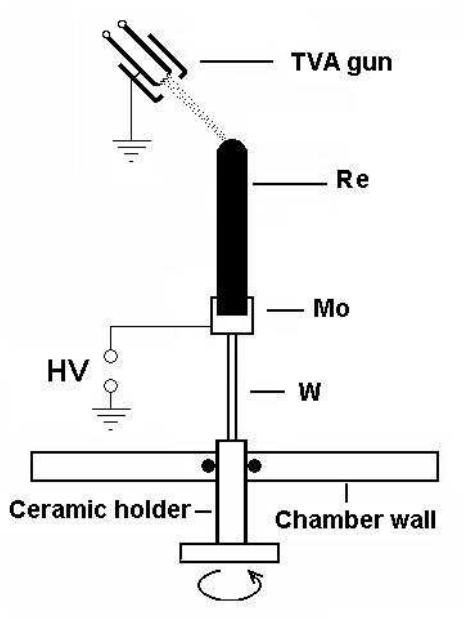

Fig. 1. Experimental setup.

The filamentary cathode of the TVA gun was made of thoriated W (W+0.2%Th) wire of 1.5 mm in diameter. The filament heating currents and applied voltages were adjusted in the ranges of 100 - 128 A and 2 - 4 V, respectively.

The upper part of the Re rod was heated up to the melting temperature, by focusing the electron flux produced by the TVA gun. After melting, a dc high voltage was applied between anode and cathode. The applied voltage was named V_d (discharge voltage) and the corresponding current between anode and cathode was named I_d (the intensity of the discharge current). Sets of V-A characteristics were recorded changing the heating current of the cathode filament.

3. Experimental results and discussion

Fig. 2 shows peculiar V-A characteristics obtained for anode voltages under pre-breakdown values.

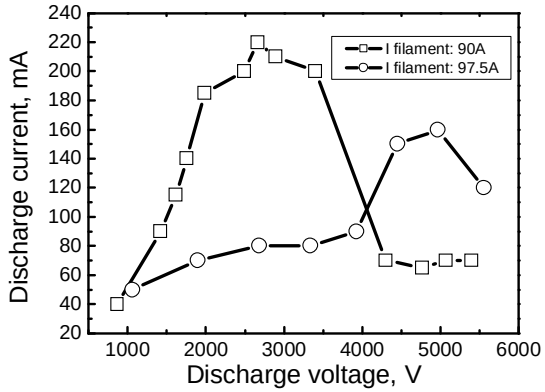

Fig. 2. V-A characteristics for 90 A and 97.5A cathode heating currents.

They represent V-A characteristics for relatively low cathode heating currents. At 90 A and 97.5 A heating currents of the filament, one can see that the increase in the anode potential leads to the increase in the thermo-electron emission current, which is expected to obey the 3/2 rule. In this case the ion generation in the anode-cathode space is zero due to the fact that the Re atom concentration in the space is not high enough to make the atom ionization possible. The discharge current I_d for the filament current of 90 A and 97.5 A begins to decrease at the anode potential of 2500 V and 5000V, respectively.

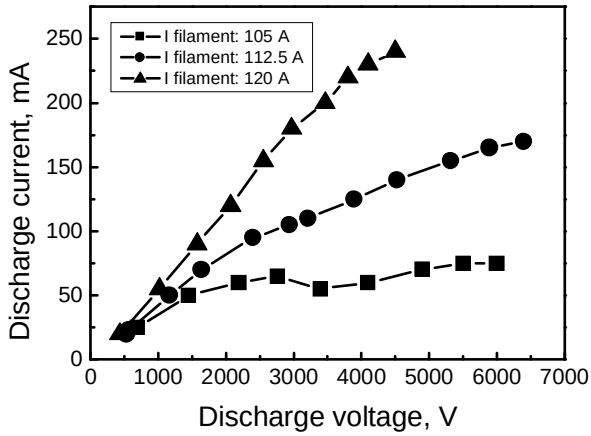

Fig. 3. V-A characteristics for 105A, 112.5A and 120A cathode heating currents.

The same tendency is observed on the other V-A curves when the cathode currents were higher but with a less definite I_d decrease due to higher filament temperatures, as can be seen in Fig. 3.

In order to explain this behavior the physical phenomenon responsible is examined theoretically. First of all the heated cathode filament is forced to emit thermo-electrons as described by the Richardson formula [5]:

$$j_e = AT_f^2 \exp\left[\frac{\Phi_W}{kT_f}\right] \tag{1}$$

where A is constant, T_f is the filament temperature, Φ_W is the electron work function and k the Boltzmann constant.

The current emission corresponds to the maximum attainable cathode-anode current in the absence of the discharge as known from the vacuum electronic tubes. Therefore when increasing the anode potential, the corresponding current (I_d) increases until it attains this value thereafter it remains constant if no discharge appears in the anode evaporated atom atmosphere. But we observed that I_d clearly decreases over a certain anode voltage V_d and this makes difficult to ignite the TVA arc because the power introduced by the electron bombardment decreases.

In order to explain and overcome this current decrease we have to take into account the anode evaporation due to the electronic bombardment.

The atomic anode evaporation current density j_a, can be determined once the anode temperature is given by the following formula [5]:

$$\log j_a = \log\left(A - \frac{B}{T_a}\right) + 22.546 - 0.5\log\left(M_{Re}T_a\right) \tag{2}$$

where A and B are given constants for every metal, M_{Re} – the atomic mass, T_a – the anode temperature.

Supposing the divergence of the atom current around the anode as zero (no atom sources, or sinks here) we can write that the total emitted atom current (by the anode) goes
through different hemisphere around the anode. In particular we can consider the hemisphere passing through the cathode position and write:

$$j_a S_a = 2\pi d^2 j_{f\,Re} \tag{3}$$

Here S_a is the anode emitting surface d – the anode-filament (cathode) distance, j_{fRe} – the rhenium atom flux striking the filament surface. Here we must infer that the atomic flux is supposed to an isotropic spread out in the space around the anode.

From the eq.3 we can deduce for the incoming rhenium atomic flux hitting the unit filament surface:

$$j_{f\,Re} = j_a S_a / \left(2\pi d^2\right) \tag{4}$$

On the other side, the rhenium atoms deposited on the filament surface are evaporated at a rate given by the formula:

$$j_{fev} = N_{Re}\gamma \exp\left(-\frac{H}{kT_f}\right) \tag{5}$$

where N_{Re} are the number of absorbed rhenium atoms, ν a characteristic vibration frequency [5]. At equilibrium we can write:

$$j_{f\,Re} = j_{fev} \Rightarrow \frac{j_a S_a}{2\pi d^2} = N_{Re}\gamma \exp\left(-\frac{H}{kT_f}\right) \tag{6}$$

where H is the equivalent of work function for a rhenium atom evaporation from the W surface.

On the filament surface the absorbed rhenium atoms change its work function. If we denote by θ, the relative filament surface covered by the rhenium atoms we can obtain a rough filament work function as:

$$\Phi = \theta\Phi_{Re} + (1-\theta)\Phi_W \tag{7}$$

where Φ_{Re} is the rhenium work function and Φ_W the work function for the uncoated filament.

Taking into account the rhenium coating influence on the filament work function we can transform equation (1) as:

$$j_e = AT_f^2 \exp\left\{-\frac{\left[\theta\left(\Phi_{Re} - \Phi_W\right) + \Phi_W\right]}{kT_f}\right\} \tag{8}$$

From this equation (which is valid for every combination of two metals) we can see that, due to the fact that $\Phi_{Re} > \Phi_W$ (Φ_{Re} = 5.1 eV and Φ_W for thoriated W is less than 4 eV) the work function of the thoriated filament is increased by rhenium atoms adsorption and this phenomenon decreases exponentially the thermoelectronic current, which is emitted by the filament.

If we consider the numbers of the absorbed rhenium atoms as given by'

$$N_{Re} = \theta N_W \tag{9}$$

where N_W is the total sites for the rhenium atoms on the unit surface of W filament (which is a constant) and θ the relative coverage. Combining (6) with (9) we can write:

$$\theta = \frac{j_a S_a \exp\left(\frac{H}{kT_f}\right)}{2\pi d^2 \gamma N_W} \leq 1 \tag{10}$$

In this case the thermoelectronic emitted current becomes:

$$j_e = AT_f^2 \exp\left\{-\frac{(\Phi_{Re} - \Phi_W)\left[j_a S_a \exp(H/kT_f)/(2\pi d^2 \gamma N_W) + \Phi_W\right]}{kT_f}\right\} \tag{11}$$

Based on the obtained formula we can interpret the V-A characteristic behaviour when increasing the anode potential as follows:

When the anode potential is small, the electronic current is increasing towards the saturated value given by the clean thoriated W filament surface:

$$j_a \Rightarrow j_e AT_f^2 \exp\left[-\frac{\Phi_{WTh}}{kT_f}\right] \tag{12}$$

which is large enough due to the fact that the Φ_{WTh} is lower than 4 eV.[6] If the filament temperature is not too high (as in Fig. 2) that is the heating current is not to high, over a certain anode potential (3500 V). The electron bombardment can increase the evaporated atom flux from the anode and therefore the filament surface coating by the rhenium atoms. As a result we can see from eq. (10) the exponent increases (especially when T_f is not too high) and j_e decreases due to the fact that Φ_{Re} - Φ_{WTh} > 1eV.

This way it can decrease the thermoelectronic emitted current and the bombarding electronic current of the anode I_d, too, taking into account that $j_e \geq I_d$.

This bombarding current decrease can decrease the total power introduced ($I_d V_d$) and the rhenium atom evaporation rate from the anode, j_a. This can decrease the first term within exponential parentheses and slightly increase the j_e value and I_d also. In fact it is observed a slight increasing tendency of the I_d for voltages over 4500V. Finally the arc discharge conditions can be attained and the simply pre-arch phenomenon considered here is no more valid.

Also from eq.(10) can be seen that when T_f is increased, j_e is increased too and the adsorbed rhenium atom influence is diminished. The $I_d = f(V_d)$ maximum is displaced towards the higher voltages (V_d) (Fig.3).

Finally, when the filament heating current is over 120 A (Fig.3) no maximum appears due to the fact that T_f is too high and the influence of the first term under the exponential parentheses of eq 10 is practically 0 and the I_d current can increase too high, j_c limiting value which is not attained here (even a slight saturation is depicted as voltages are over 4500 V).

The limiting I_d current could not be attained in case of Fig. 3 due to the fact that over 5000V the arc discharge was ignited and the simple considerations were no more valid.

In order to evaluate the anode temperatures we proceeded as follows:

The energy $I_d V_d$, which was introduced into the anode by the electron bombardment, is lost by thermal radiation, by the atom evaporation and by the thermal conduction of the anode support metallic components. Taking into account that the anodic support is a thin, long, W wire we can disregard this energy loss and consider this way the validity of the following equation:

$$I_d V_d = KT_a^4 + j_a S_a \lambda = KT_a^4 + 10^{22.546}\left(A - \frac{B}{T_a}\right)\frac{1}{\sqrt{M_{Ra} T_a}} S_a \lambda \tag{13}$$

where K is a constant for thermal radiation term, λ is the energy spent for evaporation of one Re atom and the second right side hand term is obtained from eq. 2.

One can see that I_dV_d depends on the anode temperature, T_a, value only. The unique unknown quantity is K.

In order to evaluate this we considered the electron bombarding energy, which determines the melting of the rhenium anode. The melting point of rhenium is known, namely T_{amelt} = 3450 K.

In this case:

$$I_{dm}V_{dm} = KT_{am}^4 + 10^{22.546}\left(A - \frac{B}{T_{am}}\right)\frac{1}{\sqrt{M_{Re}T_{am}}} \quad (14)$$

Knowing T_{am}, I_{dm} and V_{dm} we can derive the constant K, which can be used to represent I_dV_d as function of T_a. The obtained plot is given in Fig.4.

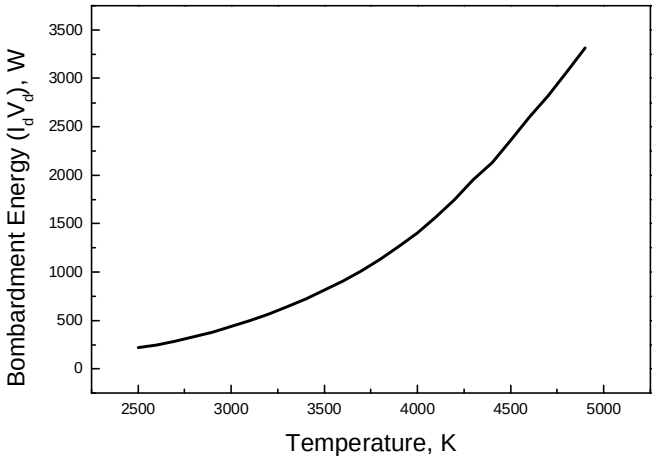

Fig. 4. The bombardment energy against anode temperature.

From this plot one can obtain the corresponding T_a temperatures for different I_dV_d values. These values can be used to determine j_aS_a values, which appear in eq.10. Knowing the T_f value as determined for a filament heating current (for example from optically measurements) we can infer the T_g values for different heating currents as in the case of the anode and using eq.10 we can infer the $H(\theta)$ values which are so far an unknown value.

Using working parameters as V_d of 2000 V, I_d of 1200 mA, filament current of 120 A and deposition time of 1 h, Re films of about 6 μm were prepared on Nb and Nb alloy substrates.

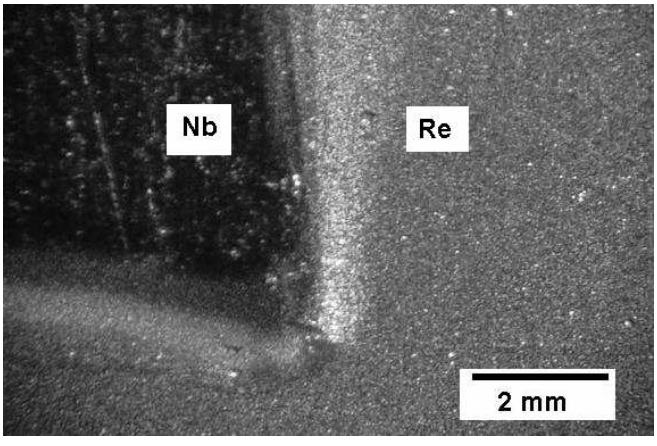

Fig. 5. Appearance of the Re film (thickness of 6.8 μm) deposited on Nb substrate.

4. Conclusions

The rhenium depositions in pre-arch conditions were considered in the present paper. Taking into account that the Re work function is higher than the thoriated W, when the evaporated Re atoms cover the filament surface, increases its work function and decreases the emitted electron current and this way the electron current flowing from the cathode to the anode too.

This is a rare encountered phenomenon due to the fact that the majority of the evaporated metals in TVA technology have a lower work function in comparison with tungsten on one side and much lower evaporation energy (H) in comparison with the rhenium one.

The simplicity of the vacuum phenomena can be used for different desorption energies determination (H) from heated tungsten, rhenium and other refractory metals used as thermoelectron emission filaments.

Using working parameters as V_d of 2000 V, I_d of 1200 mA, filament current of 120 A and processing time of 1 h, Re films of about 6 μm were deposited on Nb substrates.

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