

## **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  $\mu\text{m/h}$ .

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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.

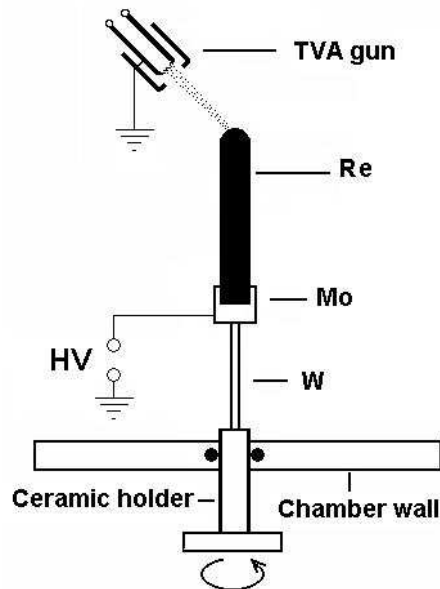


Fig. 1. Experimental setup.

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.

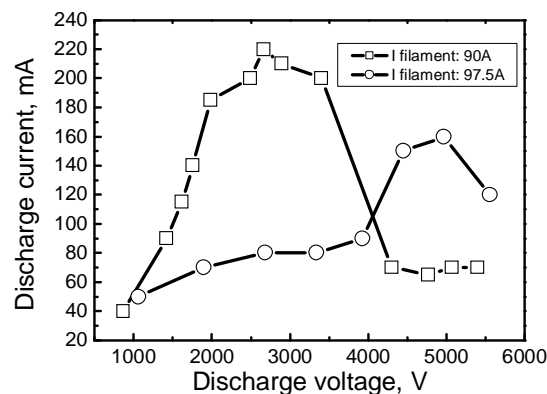


Fig. 2. V-A characteristics for 90 A and 97.5A cathode heating currents.

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.

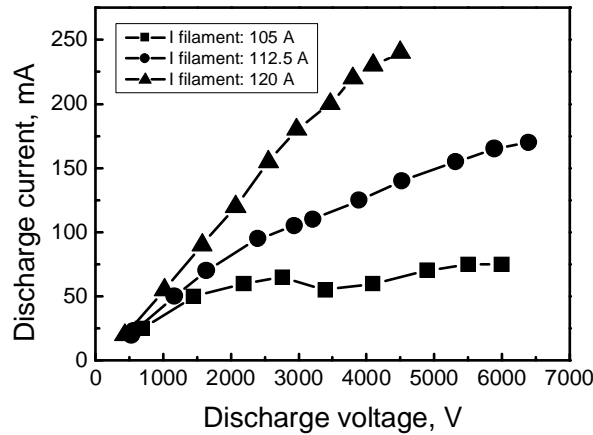


Fig. 3. V-A characteristics for 105A, 112.5A and 120A cathode heating currents.

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]:

$$j_e = AT_f^2 \exp\left[\frac{\Phi_w}{kT_f}\right] \quad (1)$$

where A is constant,  $T_f$  is the filament temperature,  $\Phi_w$  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]:

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

where  $A$  and  $B$  are given constants for every metal,  $M_{\text{Re}}$  – 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:

$$j_a S_a = 2\pi d^2 j_{f\text{Re}} \quad (3)$$

Here  $S_a$  is the anode emitting surface  $d$  – the anode-filament (cathode) distance,  $j_{f\text{Re}}$  – 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:

$$j_{f\text{Re}} = j_a S_a / (2\pi d^2) \quad (4)$$

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

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

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

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

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  $\theta$ , the relative filament surface covered by the rhenium atoms we can obtain a rough filament work function as:

$$\Phi = \theta \Phi_{\text{Re}} + (1-\theta) \Phi_{\text{W}} \quad (7)$$

where  $\Phi_{\text{Re}}$  is the rhenium work function and  $\Phi_{\text{W}}$  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:

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

From this equation (which is valid for every combination of two metals) we can see that, due to the fact that  $\Phi_{\text{Re}} > \Phi_{\text{W}}$  ( $\Phi_{\text{Re}} = 5.1$  eV and  $\Phi_{\text{W}}$  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'

$$N_{\text{Re}} = \theta N_{\text{W}} \quad (9)$$

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

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

In this case the thermoelectronic emitted current becomes:

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

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:

$$j_a \Rightarrow j_e AT_f^2 \exp\left[-\frac{\Phi_{wTh}}{kT_f}\right] \quad (12)$$

which is large enough due to the fact that the  $\Phi_{wTh}$  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 too 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  $\Phi_{Re} - \Phi_{wTh} > 1\text{eV}$ .

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,  $j_e$  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:

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

where  $K$  is a constant for thermal radiation term,  $\lambda$  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  $I_d V_d$  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  $T_{\text{amelt}} = 3450$  K.

In this case:

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

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

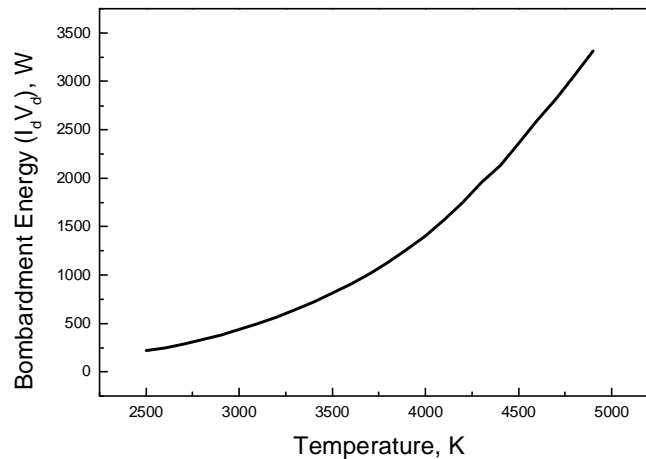


Fig. 4. The bombardment energy against anode temperature.

From this plot one can obtain the corresponding  $T_a$  temperatures for different  $I_d V_d$  values. These values can be used to determine  $j_a S_a$  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  $6 \mu\text{m}$  were prepared on Nb and Nb alloy substrates.

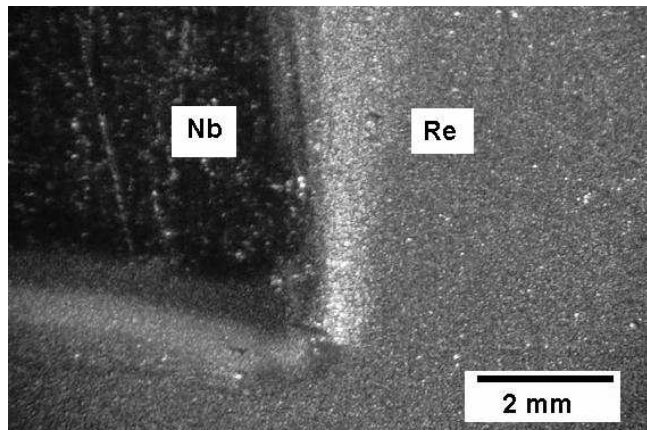


Fig. 5. Appearance of the Re film (thickness of  $6.8 \mu\text{m}$ ) deposited on Nb substrate.

#### 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  $\mu\text{m}$  were deposited on Nb substrates.

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