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Study of Refractory Metal Spectral Emissivity during High Temperature Oxidation

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A new method is developed to estimate spectral emissivity of refractory metals during high temperature oxidation. This method is based on combination of optical pyrometry and electrothermography. Spectral emissivity coefficients of oxidized refractory metals filaments are determined.

Keywords: high temperature, oxidation, tungsten, molybdenum, spectral emissivity.

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Introduction

High temperature oxidation of refractory metals (tungsten, molybdenum, titanium) is nowadays a problem of great interest due to numerous applications of these metals and their oxides in modern technologies. Molybdenum and titanium oxides are well known to be catalytically active. Tungsten oxides (powders and films) have unique physicochemical properties: electrochromic, catalytic and gas-sensing [1 - 2].

A number of approaches are developed to produce refractory metals oxides. We use so-called method of "hot filament", because it is the very convenient method to study metal oxidation in laboratory conditions. It is established that high temperature oxidation of tungsten and molybdenum is multi-stage process complicated by oxides melting and evaporation [3]. The metal temperature is a key parameter which defines chemical reaction rate and oxidation process mode (stationary or transient one). So the sample temperature control is the first priority. But we can measure only effective temperatures (brightness or color) directly by optical pyrometers. To calculate the sample thermodynamic or so called real temperature we have to know its spectral emissivity coefficient. But we as a rule have no reliable spectral emissivity data for oxidized metals. The data available from different sources vary significantly, because a spectral emissivity coefficient is not only temperature and wavelength dependent, but depends to a great extent on the surface state, temperature history and other process conditions.

During high temperature metal oxidation the surface state changes continuously, so varies its emissivity. A problem of optical pyrometry of an object with variable emissivity is still insufficiently elucidated. It should be

mentioned the research of metal particles high temperature oxidation by Dreizin which observed pronounced variations of particles luminance [4]. He explained these variations by abrupt particles heating due to metal reaction with dissolved oxygen. But there are other assumptions on this phenomenon.

I. Experimental

High temperature oxidation of refractory metals is studied by "hot filament" method. The experimental setup is presented in Figure 1. A metal filament is heated electrically by stabilized DC power supply device. Electric current and voltage drop are measured continuously. The temperature in the middle of filament is measured by optical pyrometer. The thermal radiation of hot filament is registered by digital camera through narrow-band filter. Oxide scale growth is studied by video microscopy

After the process completion we calculate $T_{el}(t)$ – so called electrothermographical temperature at successive points in time by temperature dependence of the metal specific resistivity $r(T)$ and known formula for filament electric resistance.

We take into account that initial filament temperature T_r differs from $T_0 = 273$ K, so its specific resistivity at room temperature T_r is

$$r_r = r_0 [1 + g(T_r - T_0)].$$

So we use the next expression to calculate the filament temperature $T_{el}(t)$ at a fixed point in time:

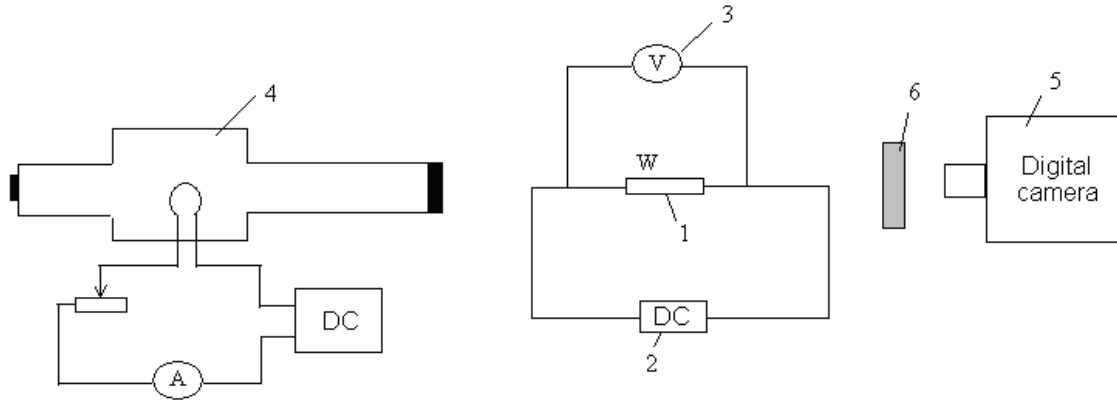


Fig. 1. Experimental setup scheme: 1. Metal filament; 2. DC power supply; 3. Voltammeter; 4. Disappearing filament pyrometer; 5. Digital camera Canon 350d; 6. Interferential filter.

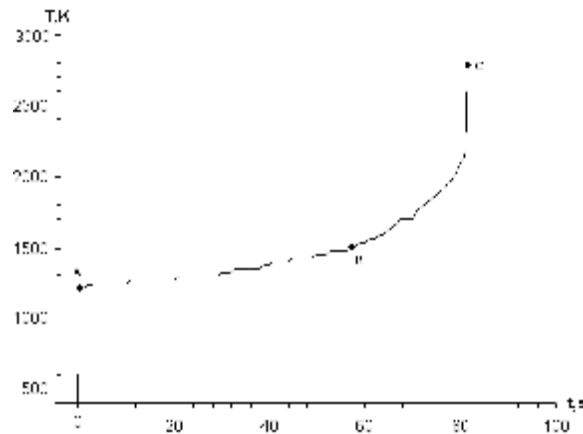


Fig. 2. A temperature history of tungsten filament ($d_0 = 210 \text{ mcm}$, $L_0 = 100 \text{ mm}$) during oxidation:
 $I = 4.5 \text{ A}$, $T_0 = 293 \text{ K}$.

$$T_{el}(t) = \left(\frac{R(t)}{R_r} - 1 \right) \left(\frac{1}{g} - T_0 \right) + \frac{R(t)}{R_r} T_r, \quad (1)$$

here $R(t)$ – the filament resistance at point in time t ;
 R_r – its initial resistance at room temperature; g –

temperature coefficient of electric resistance.

For more accurate calculations we should take into account the metal filament thermal elongation and its diameter $d(t)$ decrease due to oxidation. So the following expression is derived:

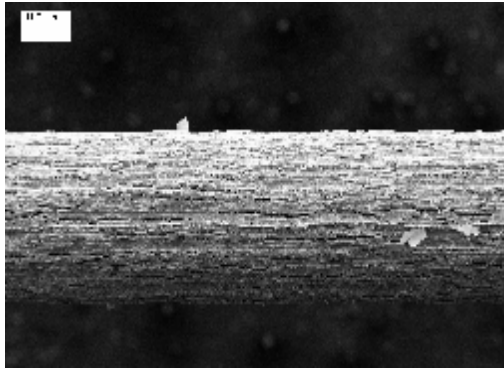
$$T(t) = \left[\left(\frac{d(t)}{d_0} \right)^2 \cdot \frac{L_0}{L} \cdot \frac{R(t)}{R_r} - 1 \right] \left(\frac{1}{g} - T_0 \right) + \left(\frac{d(t)}{d_0} \right)^2 \cdot \frac{L_0}{L} \cdot \frac{R(t)}{R_r} \cdot T_r \quad (2)$$

here: L_0 and d_0 – the initial values of filament length and diameter; L and d – the filament dimensions at the point in time t . We should note that $T_{el}(t)$ is an average value of real temperature along the filament.

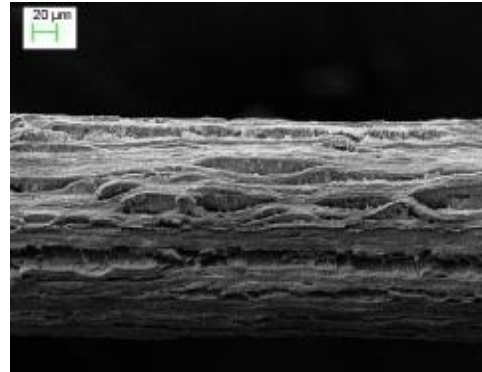
In Figure 2 the experimentally defined temperature history of the tungsten filament high temperature oxidation is presented.

We can see three successive stages [3] on the experimental curve $T(t)$ – the first stage (till point A) is characterized by temperature abrupt rise. This stage is very brief, so oxide layer is still thin at point A. During the second stage (from A to B) the temperature slowly grows up to oxide melting point, so it continues for a

relatively long time. Oxide scale thickness increases continuously and amounts to values which equals the filament initial diameter. At temperatures about $1200 \div 1400 \text{ K}$ a sublimation of oxides begins. When the filament temperature attains the oxide melting point the tungsten or molybdenum oxides begin to melt and evaporate intensively, as a result the oxidation reaction accelerates greatly. The temperature continues to rise dramatically, and the scale thickness reduces down to total disappearance, so the filament destroys quickly. As usual, there is now oxide scale nearby the filament break points. So, during the oxidation process the permanent changes occur in the stoichiometry of oxide layer, the scale thickens and cracks, sometimes oxide crystal whiskers and platelets grow on the solid scale [6].



Slightly oxidized tungsten filament



Heavily oxidized tungsten filament

Fig. 3. The images of oxidized tungsten filament.

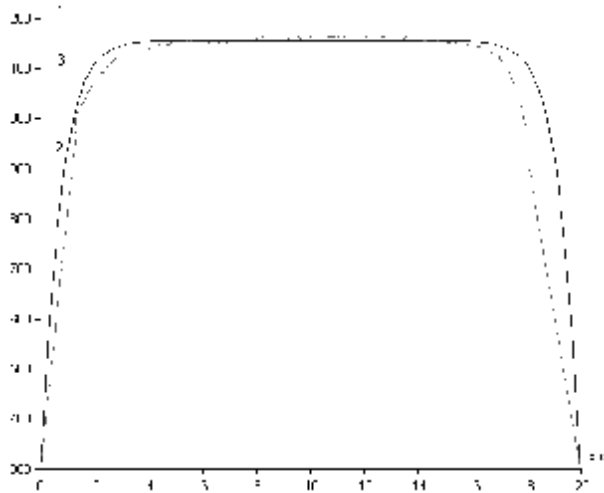


Fig. 4. Real temperature profile along a platinum filament ($d = 300 \text{ mcm}$, $L = 20 \text{ cm}$), $T_r = 293 \text{ K}$, $I = 9,3 \text{ A}$: a dashed line (1) – experimental curve; a solid line (2) – modeled curve; a straight line (3) – electrothermography.

Consequently, the spectral emissivity of the filament changes significantly. This fact should be taken into account for correct optical diagnostics. The images of oxidized tungsten filament are presented in Figure 3.

The general approach to define $e(I, T)$ is based on comparison a brightness temperature with a true temperature of an object:

$$\ln[e(I, T)] = \frac{C_2}{I} \left(\frac{1}{T_r} - \frac{1}{T_b} \right), \quad (3)$$

here C_2 – the second optical constant, $C_2 = 1,4388 \text{ m} \cdot \text{K}$, $I = 0,65 \cdot 10^{-6} \text{ m}$, T_r – a true (thermodynamic) temperature, K; T_b – a brightness temperature, K.

A developed procedure is implemented in the differing way. A brightness temperature is measured by brightness pyrometer in the middle of a filament at specific instants in time. Simultaneously we image the filament thermal radiation through narrow-band filter, and record a voltage drop across it.

Data processing includes the next steps:

1. We calculate $T_{el}(t)$ values at selected points in time.

2. Then we define the brightness temperature distribution along the filament by method of relative brightness pyrometry [3].

3. Whereupon we calculate the real temperature profile under the assumption that it is similar to the brightness temperature profile. A tabulated value $e(I, T)$ for pure metal is used as a zeroth-order approximation in the formula:

$$\frac{1}{T_r} = \frac{1}{T_b} + \frac{I}{C_2} \ln e(I, T), \quad (4)$$

here: $e(0,65, T) = 0,43$ tungsten emissivity at $T \geq 1000 \text{ K}$.

4. Finally we found the mean value \bar{T}_r of the real temperature distribution and compare it with experimental value $T_{el}(t)$.

5. Then we correct the value $e(I, T)$ and repeat steps 3 - 4.

6. In so way we find a spectral emissivity coefficient of oxidized surface by method of successive approximations. The method is illustrated in Figure 4.

In so way the emissivity values are obtained for a few refractory metals. In Table 1 some of the values

Table 1
Spectral emissivity coefficients of oxidized metals

Metal	T_r , K	T_b , K	$e(0.65)$
Platinum	1205	1123	0.27
	1237	1151	0.27
Tungsten, oxidized	1060	1021	0.45
	1114	1039	0.24
Molybdenum	927	892	0.39
	946	912	0.41

Table 2
The experimental values $e(I, T)$ for tungsten filament at successive] points in time

The stages of Oxidation	Oxidation time, s	T_r , K	T_b , K	$e(0.65)$
1	30	1320	1270	0.4
2	180	1315	1160	0.11
3	240	1440	1238	0.08

obtained are presented. To verify our method we use a platinum wire (length 20 cm, diameter 300 μm), heated electrically. The defined value of $e(0.65, T)$ value is in good agreement with reference data $e(0.65, T) = 0.3$ for the temperature range $1250 \div 1750$ K.

In Table 2 the obtained data of spectral emissivity for tungsten filament during oxidation are presented.

We obtain the error estimate by differentiation expression (3):

$$\frac{\Delta e}{e} = \frac{C_2}{I} \cdot \left(\frac{\Delta T_r}{T_r^2} + \frac{\Delta T_b}{T_b^2} \right). \quad (5)$$

Then the expression (5) is simplified:

$$\frac{\Delta e}{e} \approx \frac{C_2}{I \cdot T} \cdot (dT_r + dT_b), \quad (6)$$

here dT_r and dT_b are the relative errors of true and brightness temperatures measurement. We use precise brightness pyrometer with disappearing filament, so $dT_b \approx 0.002$. The real temperature measurement is

less accurate: $dT_r \approx 0.01$. In so way the total relative error is about 10%, that is quite adequate accuracy for spectral emissivity measurement, because a logarithm of $e(I, T)$ is used for calculations as seen in equations (3) – (4).

It is found that drastic decrease of $e(I, T)$ is observed at the beginning of the second stage of oxidation process when scale thickness attains value about some micrometers. The next abrupt change – emissivity rise occurs immediately before filament breaking due to full cleaning of metal surface. Unfortunately, it is very rush, so we couldn't register the corresponding voltage drop and to define the temperature values. Corresponding changes in the brightness are observed visually. It should be noted that the total emittance changes inversely: at the beginning of oxidation $e(T)$ rises at least threefold, and at the end it decreases as much. Between these two points the smooth variations of spectral emissivity and total emittance take place. It is found that a lot of factors affect the oxide layer stoichiometry and structure: ambient gas composition, a metal surface contamination, temperature history and so on. As a result spectral emissivity depends strongly on process conditions, so defined values of $e(I, T)$ may vary in different experiments.

Conclusions

Correct optical diagnostics of high temperature processes requires taking into account permanent surface transformations due to chemical and phase transformations, which influence the spectral and total emissivity values. The new simple method is developed for defining spectral emissivity coefficient of metal surface during high temperature oxidation. The coefficients of spectral emissivity are found for some metal filaments (W, Mo, Pt).

It is shown that coefficient of spectral emissivity decrease significantly during the second stage, which is limited by oxide melting point.

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- [1] E.B. Franke and oth. J. of Appl. Phys, 88(10), 577 (2000).
- [2] A. Ponzoni, E. Comini and G. Sberveglieri. Appl. Phys. Lett. 88, 203101 (2006).
- [3] S.G. Orlovskaya, M.S. Shkoropado, F.F. Karimova. Physics and Chemistry of Solid State 13(4), 1000 (2012).
- [4] A.E. Sheindlin (ed.). Emissivities of Solids. (Handbook. Energy, Moscow, 1974).
- [5] G. Teodorescu. Radiative Emissivity of Metals and Oxidized Metals at High Temperature. Dissertation (Auburn University, 2007).
- [6] E.L. Dreizin, A.V. Suslov, M.A. Trunov. Combust. Sci. and Tech. 87, 45 (1993).
- [7] M.S. Shkoropado, S.G. Orlovskaya, F.F. Karimova. Ukrainian Journal of Physics 56(12), 1312 (2011).

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Визначення випромінювальної здатності тугоплавких металів у процесі високотемпературного окислення

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Розроблено нову методику визначення коефіцієнту спектральної випромінювальної здатності металів безпосередньо у процесі високотемпературного окислення. Методика базується на одночасному застосуванні методів оптичної пірометрії та електротермографії. Знайдено коефіцієнти спектральної випромінювальної здатності окислених дротиків тугоплавких металів (вольфраму, молібдену) у процесі окислення.

Ключові слова: високотемпературне окислення, вольфрам, молібден, спектральна випромінювальна здатність.