*Thermochimica Acta*, 133 (1988) 299–304
Elsevier Science Publishers B.V., Amsterdam


# INSITU MEASUREMENTS OF LAYER THICKNESS DURING OXIDATION OF TITANIUM

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## ABSTRACT

Thermal radiance measurements are described as a method well suited for insitu measurement of layer thickness during the oxidation of titanium at temperatures between 700 °C and 1000 °C. The results confirmed the parabolic function of the oxide growth with a constant C increasing up to 0.029 $\mu m^2/s$ with increasing oxidation temperature.

## INTRODUCTION

The thermal radiation properties of metallic surfaces are strongly dependent on their topography. Amongst the roughness, oxidation has the most important influence on the variation of the reflectance respectively emittance of metals. By means of the classic electro-dynamic-theory the reflectivity of a thin film on metals can be calculated as a function of its thickness if the optical constants (index of refraction n and extinction coefficient k) both of the metal and the oxide film are known and constant during the oxidation process ( ref.1). Emittance measurements, carried out by the authors on oxidizing steel samples (ref.2) have clearly demonstrated that the observed variation of the spectral emittance could be related to the increase of the oxide layer thickness. These results are encouraging to apply

*Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988*
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radiation measurement techniques to in situ measurements of film thickness during oxidation processes. In principle two methods are possible:

a) irradiation of the metallic surface by a monochromatic light source (e.g. laser beam) and measurement of the ratio of the reflected to the incident radiation flux.
b) at temperatures above 500°C, at which oxidation usually occurs, the spectral radiance can be directly measured with the aid of a linear detector.

## EXPERIMENTAL TECHNIQUE

In order to observe the oxide growth on titanium the direct radiance measurement technique has been applied by using a specijally developed spectral pyrometer (ref.3). This 'Linearpyrometer' uses a silicon photo detector, whose photocurrent $I_{ph}$ is proportional to the radiance and therefore the Wien's equation can be used for the data evaluation:

$$I_{ph} = K_{\lambda}(\varepsilon_{\lambda}/\lambda^{5}) \cdot \exp(-c_{2}/\lambda T), \qquad (1)$$

where $\lambda$ is the effective wavelength, which is given by an interference filter. The pyrometer is equipped with two filter wheels both containing six places for such filters ranging between 0.5 µm and 0.9 µm. The described measurements were carried out at $\lambda$ = 0.71 µm $c_2$ is the second radiation constant (= 1.4380 µmK) and $K_{\lambda}$ is the calibration factor of the 'Linearpyrometer', which only depends on the chosen wavelength. The spectral emittance $\varepsilon_{\lambda}$ and the temperature T of the sample are potential variables in Eq.(1). By measuring T using an independent technique - e.g. with the aid of a thermocouple - $\varepsilon_{\lambda}$ can be calculated from the measured photocurrent $I_{ph}$. According to the Kirchoff's radiation law the reflectance $\rho$ is calculated using the relation

$$\rho = 1 - \varepsilon \qquad (2)$$

For the determination of the oxide thickness, the measured reflectance values have to be compared with those which are calculated as a function of layer thickness. As indicated in Fig. 1 a film on metal leads to interferences. Therefore the calculated reflectance, Fig. 2, shows maxima and minima with increasing thickness.

## RESULTS AND DISCUSSION

Measurements were carried out on samples with 30 mm diameter punched out from a 3 mm thick cold rolled tantalum metal (99,86% pure). The samples were heated in an inert atmosphere up to a certain temperature and after a stable temperature was reached the oxidation process was initiated by switching the gas flow from argon to dry air (dew point = -45°C). As Fig. 3 shows, the spectral emittance $\varepsilon_\lambda$ ($\lambda$ = 0.71 µm) is nearly 0.5 before the oxidation. At the dashed line the oxidation begins, resulting in a variation of the emittance. At 990 K the oxidation and thus the increase of the emittance is extremely moderate. At a temperature, which is 100 K higher, the emittance reaches the first maximum after a few seconds and a second maximum appears after about 40 s. These correspond to the first two maxima in Fig. 2.

The positions of the maxima and minima marking distinct layer thicknesses as given in Tab. 1. For the calculation of the thickness the optical constants were taken from the literature (ref. 4 to 10). With the exception of ref. 5 all reported values result from room temperature measurements. The mean values n = 2,6 and k = 3,5 for titanium and n = 2,53 and k = 0,33 for $TiO_2$ were used for the calculations. The resulting emittance as a function of oxide layer thickness is plotted in Fig. 2 whereby the index of refraction of $TiO_2$ is varied between 2.4 and 2.6. This leads to a ± 5 % variation of the position of the maxima and minima. Because

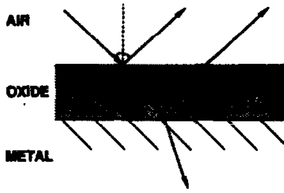


Fig. 1: Model of the radiation behaviour of thin films on metals

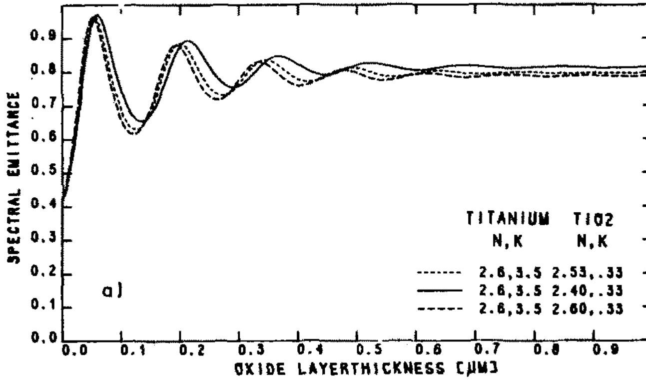


Fig. 2: Spectral emittance $\varepsilon_\lambda(\lambda = 0.71\ \mu m)$ of a $TiO_2$ film on titanium, calculated as a function of layerthickness

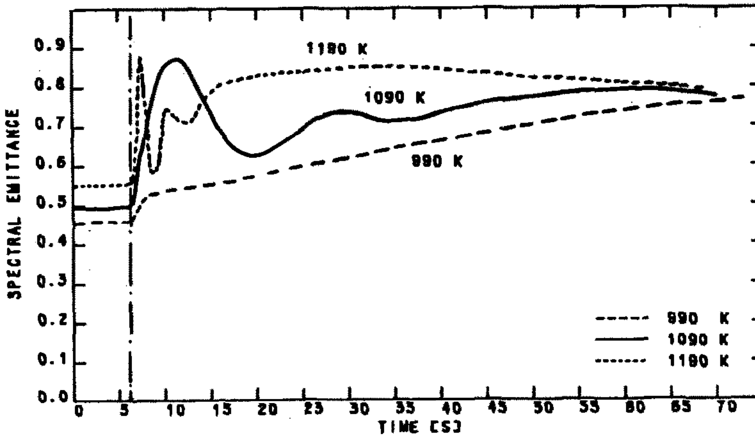


Fig. 3: Spectral emittance $\varepsilon_\lambda(\lambda = 0.71\ \mu m)$ measured on oxidizing titanium samples as a function of time at different annealing temperatures

all other optical properties do not cause remarkable changes of the positions of the extreme values but only of the amplitude. The accuracy of the index of refraction of the film is the magnitude, which is limiting the accuracy of the proposed method to measure oxide thickness The reproducibility is below 1 % and the resolution is around 0.01 µm.

Tab. 1: Calculated thicknesses of a $TiO_2$-layer at the maxima and minima of the spectral emittance $\varepsilon_\lambda$

| 1. Max | 1. Min | 2. Max | 2. Min | 3. Max | |
|---|---|---|---|---|---|
| 0.055 | 0.125 | 0.200 | 0.270 | 0.345 | µm |

The squares of the thickness values plotted versus the time at which the extreme values of the emittance appear in Fig. 3 form straight lines whereby the gradient increases with increasing oxidation temperature. This confirms the expected parabolic function of oxide growth (ref. 11). According to that, the thickness d as function of time is

$$d^2 = C \cdot t. \tag{3}$$

The growth constants C in Eq. (3) can be determined from the measured $\varepsilon_\lambda = f(t)$ - curves by linear regression. The results are listed in Tab. 2 for the investigated oxidation temperatures.

Tab. 2: Growth constants for the oxidation of cold rolled titanium, oxidized on air

| Oxidation Temperature T [K] | Growth Constant C [µm²/s] x 10³ |
|---|---|
| 990 | < 0.05 |
| 1090 | 1.81 |
| 1190 | 20.4 |
| 1290 | 29.2 |

## CONCLUSION

Radiance measurements are suited for *in situ* measurements of the thickness of oxide layers in the range where the films are optically thin. The accuracy is mainly influenced by the knowledge of the index of refraction of the oxide. Measurements of the optical constants especially at high temperatures are needed to improve the accuracy in correlating spectral emittance to oxide thickness.

## ACKNOWLEDGEMENT

The described work was financially supported by the Arbeitsgemeinschaft industrieller Forschungsvereinigungen e.V., AIF.

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