

# Oxidation of Chromium

Oxidation of chromium is very simple as it usually forms a single oxide  $\text{Cr}_2\text{O}_3$ . It is a p-type of oxide with  $\text{Cr}^{3+}$  ions diffusing outward. Since the defect concentration is so low that even at high temperatures, the diffusion is dominated by GB's.

Oxidation follows a parabolic law as long as the scale remains firmly attached to the metal and no cracks or fissures develop through which oxygen can pass. Growth law can be given as:

$$W^2 = K_p t + C$$

When chromium is oxidised in air, the scale consists of a nitride (possibly  $\text{Cr}_2\text{N}$ ) next to metal and oxide interface, followed by chromium oxide at the outer side. Since nitriding is a more rapid process in chromium than oxidation, the nitride layer probably forms first and is then covered with oxide. The rate of scaling is again parabolic similar to that of oxidation

The rate controlling process is the diffusion of chromium ions through the nitride layer, followed by oxide layer.

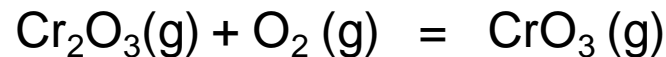
Preoxidation of chromium in oxygen followed by exposure to nitrogen at 1000°C shows that the nitride formation was variable, which perhaps reaches through pores and cracks in the oxide.

Similarly when nitrided chromium was oxidised, oxygen reacted with nitride and released nitrogen which diffused into the matrix and established gradient pushing nitrides inwards.

## Oxidation of Chromium with Simultaneous Volatilisation

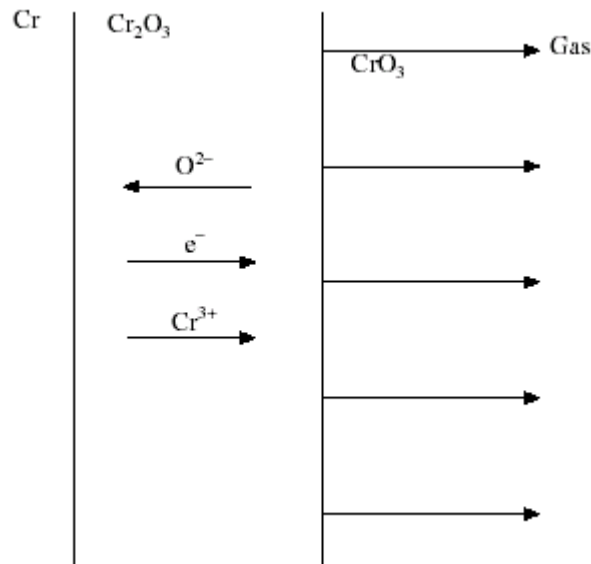
Chromium is one of the most important alloying element in steels, stainless steels And many Ni base alloys and super alloys. The oxidation protection is due To the formation of protective chromia layer.

This chromia layer, however is protective till a temperature of 900°C after which It dissociates into a  $\text{Cr}^{+6}$  oxide which is volatile and hence destabilise the scale



This reaction is possible above 900°C at high oxygen partial pressure

How this will affect the oxide scale has been treated her:



Schematic of Chromia De-stabilization

$$\frac{dx}{dt} = \frac{k'_d}{x} - k'_s \quad (6.28)$$

where  $k'_d$  is a constant describing the diffusive process and  $k'_s$  describes the rate of volatilisation. This equation can be re-arranged to yield

$$\frac{dx}{\frac{k'_d}{x} - k'_s} = dt \quad (6.29)$$

which upon integration yields:

$$\frac{-x}{k'_s} - \frac{k'_d}{k'^2_s} \ln(k'_d - k'_s x) + C = t \quad (6.30)$$

where  $C$  is the integration constant to be evaluated from the initial conditions. Taking  $x = 0$  at  $t = 0$

$$t = \frac{k'_d}{k'^2_s} - \frac{k'_s}{k'_d} x - \ln\left(1 - \frac{k'_s}{k'_d} x\right) \quad (6.31)$$

Initially, when the diffusion through a thin scale is rapid, the effect of  $\text{CrO}_3$  volatilisation is not significant, but as the scale thickens, the rate of volatilisation becomes comparable to and then becomes equal to the rate of diffusive growth. This situation results in a parabolic oxidation to a limiting scale thickness,  $x_0 = 0$  for which  $dx/dt = 0$  which is shown schematically in Fig. 6.9. Setting this condition in Eq. 6.28 yields:

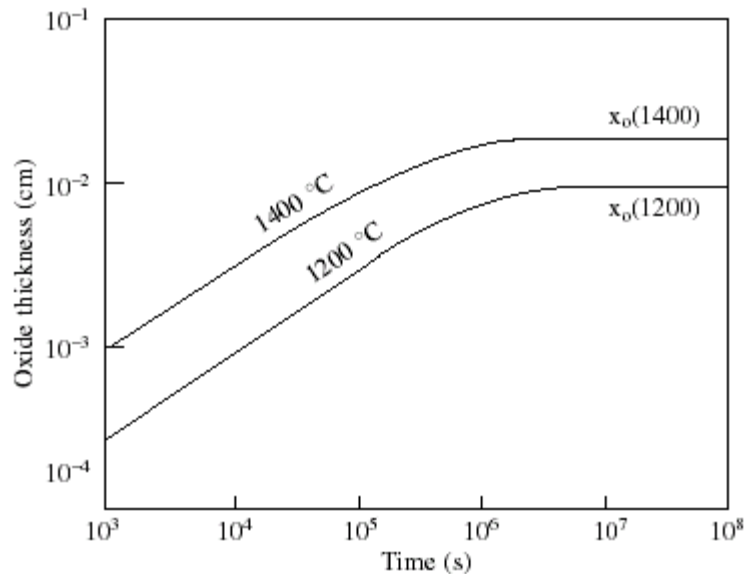
$$x_0 = -\frac{k'_d}{k'_s} \quad (6.32)$$

If instead of weight loss due to volatilization  
The total metal loss (y) is measured the  
Modified equation is as follows:

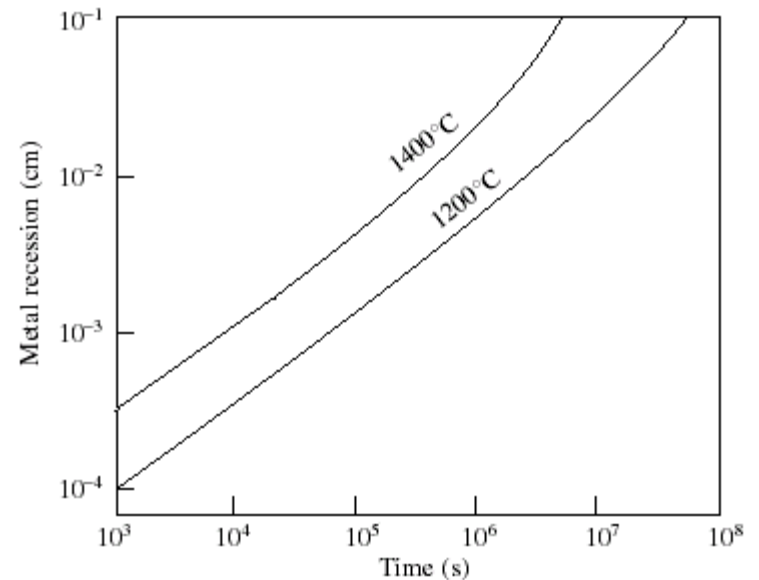
$$\frac{dy}{dt} = \frac{k_d}{y} + k_s$$

Which on integration gives

$$t = \frac{k_d}{k_s^2} \left[ \frac{k_s}{k_d y} - \ln \left( 1 + \frac{k_s}{k_d y} \right) \right]$$



And now if you see the plot, it clearly  
Shows destabilization after sufficient  
 $\text{CrO}_3$  has been evaporated



# Effect of Oxygen dissolution

The oxygen may be present in the metals as interstitially dissolved atoms, molecular gas or in the form of oxides. The interstitially dissolved oxygen may exhibit

- ordering, and the tendency for this increases with increase in oxygen content and decrease in temperature.
- Internal oxide formation
- ( Both of these are detrimental to metal properties)

The extent of the oxygen solubility varies greatly for different metals. The solubility of oxygen in the  $\alpha$  phase of Ti, Zr and Hf amounts to about 30, 28 and 20 atom % respectively.

The solid solubility in group VA metals is considerably smaller; it increases with temperature and for Nb and Ta, it amounts to about atom 5% at 1500°C.

For BCC metals, the value of diffusion coefficient,  $D_o$  often ranges between 0.001 to 0.01 with values of the activation energy for oxygen diffusion in BCC metals generally range from 105 to 145 kJ/mole.

The activation energies in HCP metals are considerably higher and are of the order of 180 – 220 kJ/mole.

## Metals with Significant Oxygen Dissolution during Oxidation

Whenever, a metal which has strong oxygen solubility is oxidized, its total Weight gain is due to oxide scale formation as well due to oxygen dissolved In the metal. Hence the treatment here tries to explain how these two can Be taken into account

Assumption : Both oxygen dissolution and oxidation follow parabolic law

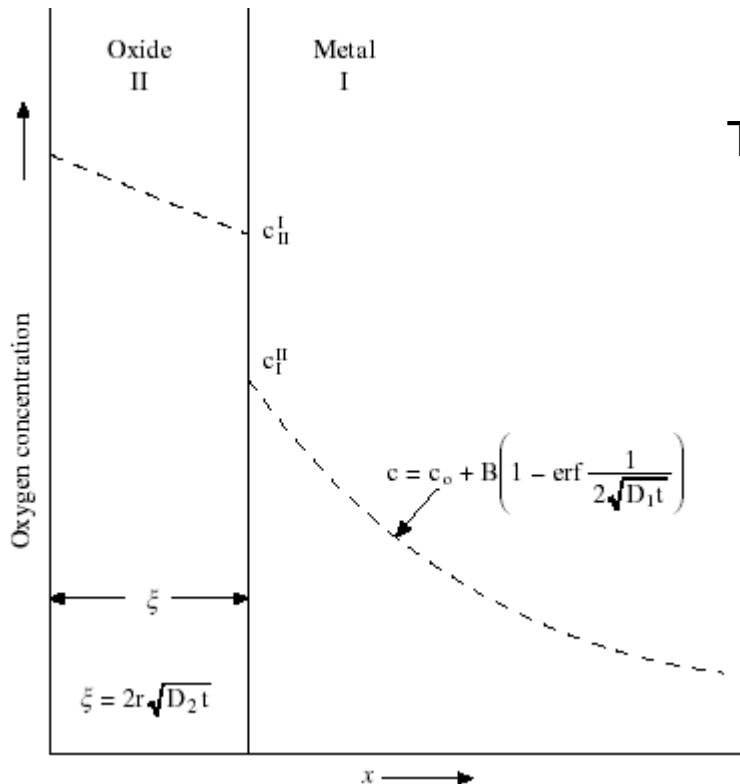
Weight due to metal oxidation  $w_1 = (kt)^{1/2}$   
 Weight due to oxygen dissol.  $w_2 = (kt)^{1/2}$

Total weight  $W = w_1 + w_2 = (K_p t)^{1/2}$

$$K_p^{1/2} = k_1^{1/2} + k_2^{1/2}$$

$$\frac{dW}{dt} = -D_2 \left( \frac{dc}{dx} \right) \quad x < \xi$$

$$= (c_2 - c_1) \frac{d\xi}{dt} - D_1 \left( \frac{dc}{dx} \right) \quad x > \xi$$



$$c = c_0 + B \left( 1 - \operatorname{erf} \left( \frac{x}{2} \sqrt{Dt} \right) \right) \quad \text{for } x > \xi$$

where  $B$  is a constant and  $c_0$  is the original oxygen content in the metal.

The parabolic growth of oxide thickness can be expressed by

$$\xi = 2\gamma(D_2t)^{1/2}$$

where  $\gamma$  is a constant. Integration of Eq. 6.40 gives

$$W = 2\gamma(c_2 - c_1)\sqrt{D_2t} + 2\frac{B}{\sqrt{\pi}}D_1 \exp \left( -2\gamma^2 \frac{D_2}{D_1} \right) t^{1/2}$$

The overall weight gain as a function of time may be written as

$$W = (K_p t)^{1/2} = (k_1^{1/2} + k_2^{1/2})^{1/2}$$

where

$$k_2 = 2\gamma(c_2 - c_1)\sqrt{D_2}$$

and

$$k_1 = \frac{2BD_1}{\pi} \exp \left( -\gamma^2 \frac{D_2}{D_1} \right)$$

By combining Eqs. 6.40 and 6.41 we get the value of the constant  $B$  as

$$B = \frac{c_1 - c_0}{1 - \operatorname{erf}(\gamma D_2 / D_1)}$$

# Oxidation of Titanium

Ti forms several oxides:  $\text{Ti}_2\text{O}$ ,  $\text{TiO}$ ,  $\text{Ti}_3\text{O}_3$ ,  $\text{Ti}_3\text{O}_5$  and  $\text{TiO}_2$ .

However, oxidation in oxygen at near atmospheric pressure and below about  $1000^\circ\text{C}$ , only  $\text{TiO}_2$  is formed. But at higher temperatures, particularly at reduced oxygen pressures, lower oxides are expected to be formed.

Titanium exists in two allotropic modifications. The low temperature  $\alpha$  form has an *hcp* structure and the high temperature  $\beta$  form, a *bcc* structure.

The transition between two phases occurs at  $882^\circ\text{C}$ .

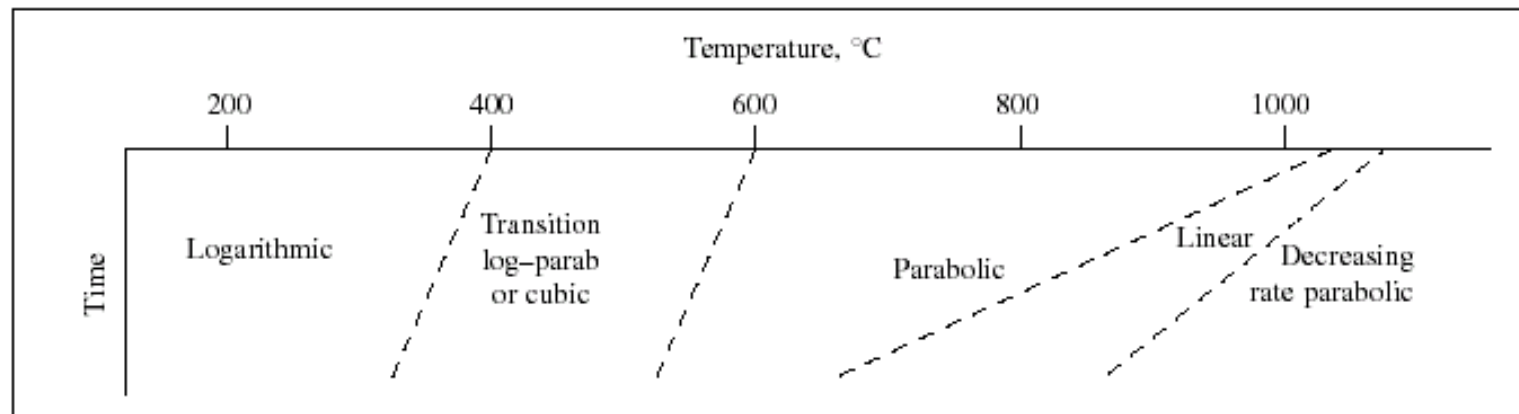
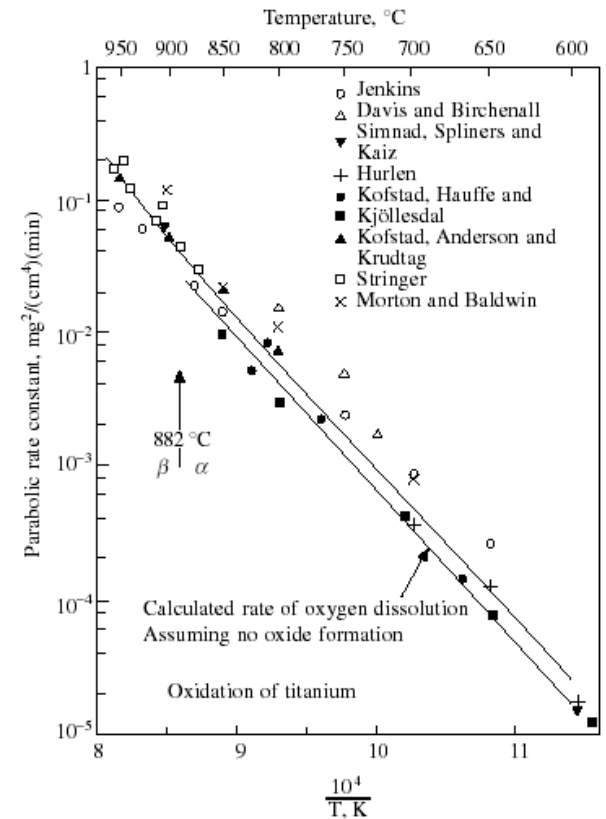
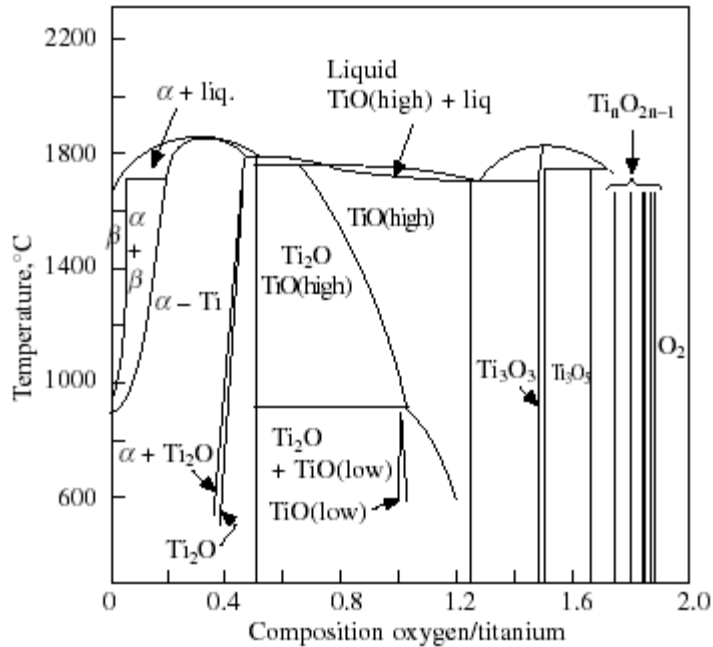
The solubility of oxygen in the  $\alpha$  phase amounts to about 30 at.% and varies little with temperature.

The solubility of oxygen in the  $\beta$  phase increases with temperature and is about 8 at.% at  $1700^\circ\text{C}$ .

The  $\alpha$  phase is stabilized by oxygen dissolution.



# Oxidation of Titanium



# Mechanism of Ti Oxidation

The defect structure of rutile suggests that there are both types of defects in  $\text{TiO}_2$ :  $\text{O}^-$  and interstitial  $\text{Ti}^{4+}$ .

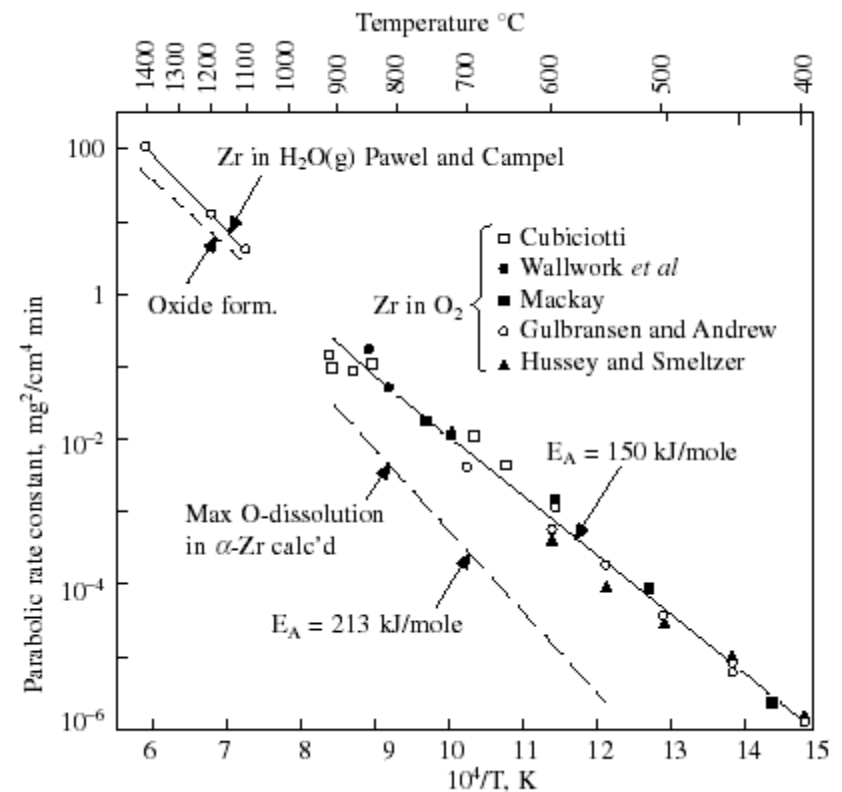
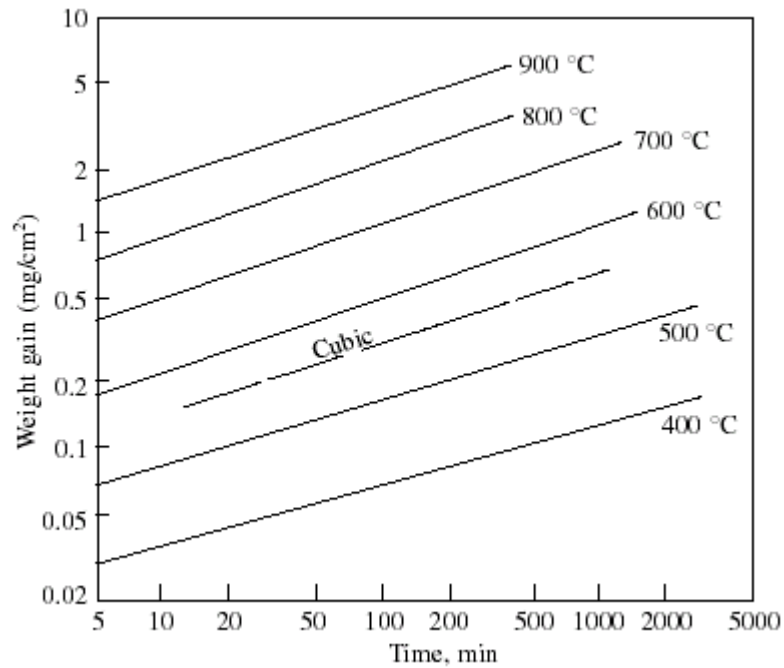
In terms of non-stoichiometry, rutile can be expressed as  $\text{Ti}_{1+y}\text{O}_{2-x}$ .

Interstitial titanium ions predominate at low oxygen pressures and high temperatures, and oxygen vacancies become important at high oxygen pressures and low temperatures.

Mechanism of oxidation, appears to be the formation of rutile by outward diffusion of titanium ions in an inner layer and inward diffusion of oxygen ions in an outer part of the scale confirmed by marker studies also.

At  $1000^\circ\text{C}$ , parabolic rate turns out to be linear - due to either accumulated stress or due to excessive oxygen dissolution

# Oxidation of Zirconium



## Mechanism of Oxidation and Oxide Type

ZrO<sub>2</sub> being an *n*-type semiconductor, oxygen vacancies are the predominant defects below 1500°C. The scale grows by oxygen transport.

ZrO<sub>2</sub> may exist in three forms: monoclinic below 1000 to 1200°C; tetragonal between 1000–1500°C; and cubic above 1500°C. The transformation between the monoclinic and tetragonal form occurs in a range of temperatures and depends upon the impurities in the metal.

Oxide films formed below 1000°C generally have monoclinic ZrO<sub>2</sub>.

## Mechanism of Breakaway Oxidation

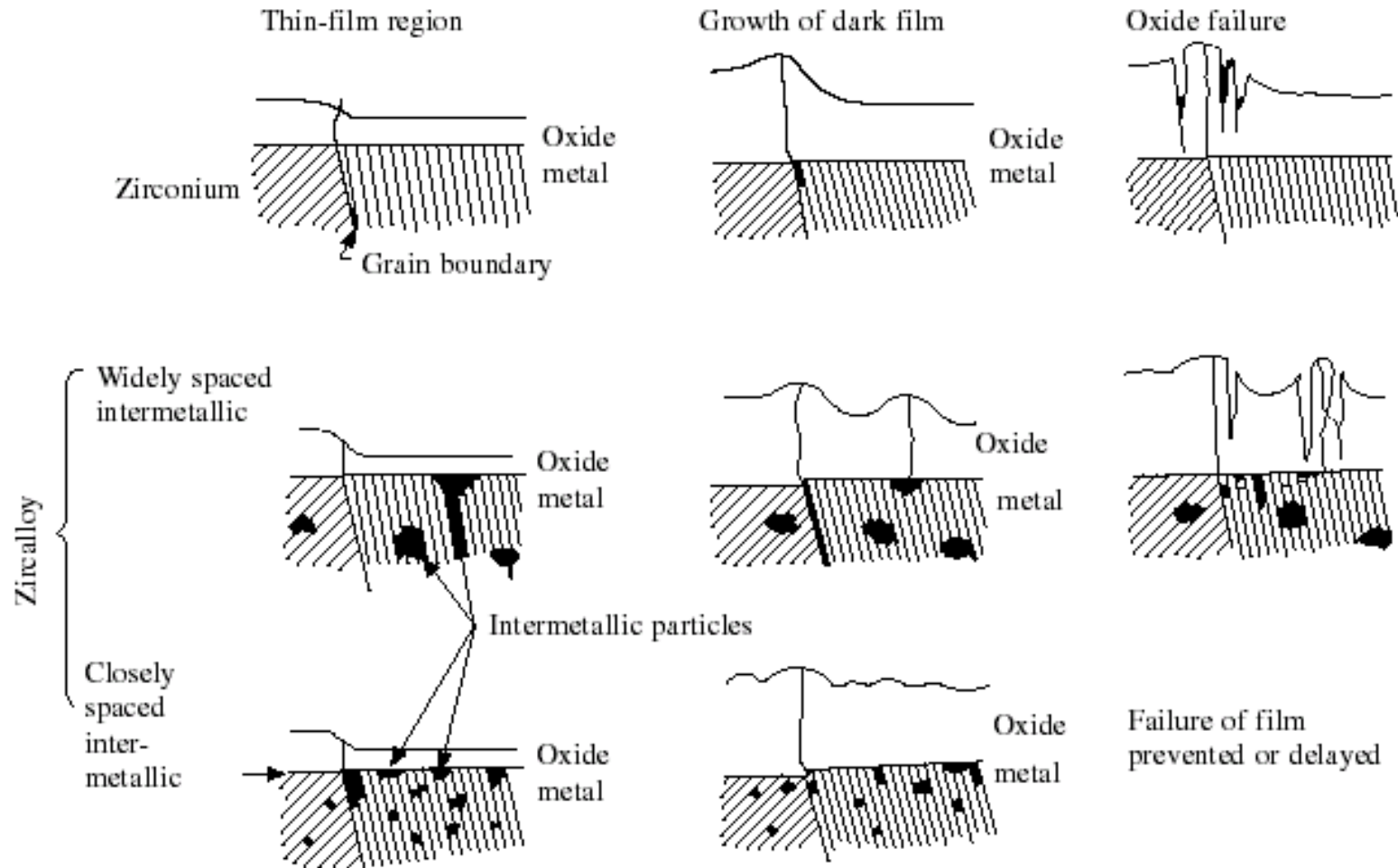
Occurs when adherent grey colour ZrO<sub>2</sub> changes to white oxide

Cox has proposed that inhomogeneous distributed impurities in the metal, alloy additions or presence of intermetallics play an important role.

It is reported that the breakaway oxidation is delayed in a very pure zirconium metal. The presence of impurities may provide misorientation in the oxide at grain boundaries and in inhomogeneous regions, through which diffusion is expected to take place.

Such transport mechanism may lead to small scale local variations in the growth rate, which in turn, result in stresses and nucleate failure in the oxide. According to Cox, the number of such nucleation sites increase with time.

# Breakaway Oxidation Mechanism of Zirconium



## Oxidation of Chromium

