# Minor alloying during surface oxidation of stainless steel

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Alloying elements in stainless steel have been found to influence the passive protective film on stainless steel surface. There are two major rate limiting steps involved viz. high field assisted ionic transport (eqn 1) through the oxide layer and charge transfer at metal/film or film/electrolyte interface (eqn 2). The second process also leads to point defects.

$$\frac{\partial d}{\partial t} = r_g K_1^{hf} e^{BU/d} \quad (1) \quad ; \quad \frac{\partial d}{\partial t} = K_1^{if} e^{K_2(\Delta U - E_o \Delta d)} \quad (2)$$

where d is the film thickness, $r_g$ is the growth fraction, $K_1^{hf}$ , high filed constant, B the oxide specific constant and U is the applied potential, $E_o$ is the electric filed . The oxide layer on the SS surface is never a static one and is always changing in thickness and composition either due to adsorption or desorption which is triggered by surface segregation due to minor allying as well as annealing. According to Pilling Bedworth Ratio (PBR) concept, which is the ratio of volume of oxide to volume of metal, the value should be between 1 and 2 for a protective film. Hence time plays an important role here. The passive film has been assumed to be a sort of hydrous oxide which has more or less colloidal character.

Passive refers to unreactive and is a protection towards further oxidation, moisture, The passive layer can get damaged chemically or due to physical abrasion and due to the effect of temperature. The rate of self recovery is another important aspect. Slower rates if recovery and reformation of the passive leads to rusting. Stainless steel although possessing a general resistance to corrosion, are prone to pitting corrosion that usually occurs in environments containing chlorides. Strain enhanced dissolution effects in the corrosion-fatigue failure has also been observed.

Heat treatment of stainless steel leads to loss in the martensitic phase altering the bulk properties. An electrochemically induced annealing however removes the brittle martensitic phase without causing any major change in the hardness.

Passive films as well as thermally grown oxide films have semiconducting properties. They are composed of p-type and n-type layers, regardless of the presence of negative resistance in the films. At the passive film – electrolyte interface, Mott Schottky relation is used which takes into account the contribution of Helmholtz layer capacitance, $C_H$

$$\frac{1}{C^2} = \frac{1}{C_H^2} + \frac{2}{\epsilon \epsilon_o q N_q}\left(U - U_{FB} - \frac{k T}{q}\right) \quad (3)$$

where Nq is the donor /acceptor density, $\in$ is the dielectric constant of the passive film, $\in_o$ is the vacuum permittivity, q is the elementary charge ( e or h), k is the Boltzmann constant, T is the absolute temperature and $U_{FB}$ is the flat band potential. There is a photocurrent ($I_{ph}$) going through the passive film whose ratio with the incident photon flux is called Quantum Efficiency.

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