

**Studies on Oxidation behavior of Nickel based Super Alloy(Inconel 600)**
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**Abstract**

The most important form of corrosion is the attack by the accelerated oxidation which takes place when the air or fuel is contaminated with certain impurities. This is a serious problem in aircraft, marine, industrial and land-base gas turbines. The formation of porous non-protective oxide scales at the surfaces and sulphides at the substrate will lead to material degradation at high temperature applications. This type of attack is generally referred by 'hot corrosion' which is of two types namely type-I and type-II. This paper attempts exclusively to explain the behavior of oxidation on Inconel 600, a super alloy used for high temperature applications. The kinetics of oxidation are determined and discussed.

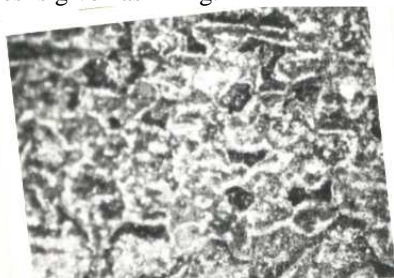
**Keywords:** Oxidation, growth stress, thermal stress, kinetics of oxidation, hot corrosion.

**Introduction**

The oxide formed first on alloys at ambient temperature is usually contaminated by impurities from the atmosphere or substrate, such as chlorine or sulfur, when a freshly prepared surface is exposed to nominally dry oxygen of air. These contaminated oxides are not the corrosion products formed by action involving thin electrolyte layers when a metal or alloy is attacked by a moist environment as in the rusting of iron.

Oxide development on a clean or contaminated, freshly prepared metal surface involves absorption of gas, appearance of two-end three-dimensional nuclei, nuclei coalescence to give a complete, reasonably uniform oxide film, comprising grains and subsequent film thickening by metal or oxygen transport through the film, usually diffusion or ion migration.

For most metals, oxidation in spontaneous because the free energy change is large and negative. The development of oxide layers along with the grain boundaries is given as in Fig.1



**Fig.1 Oxidation of the alloy with oxide layers at 7000c  
24 hrs.**

**Review of earlier works on Oxidation of alloys**

T.I.Barry and A.T.Dinsdale<sup>1</sup> has arrived the following conclusion as they were examined the Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> formation on nickel, cobalt, and iron based alloys.

- i. Chromium and particularly aluminum have greater affinity for oxygen nickel, cobalt or iron. eg: When a Ni-Cr alloy is oxidized, Cr<sub>2</sub>O<sub>3</sub> rather than NiO formation is favored thermodynamically although whether it develops as the steady-state scale is determined by various other factors.
- ii. A further important quantity is  $\Pi_{mo}$  the equilibrium dislocation pressure of MO is given by  $\Pi_{mo} = \exp(\Delta G^{\circ}/RT)$  where  $\Delta G^{\circ}$  is the standard Gibbs energy of formation of the oxide(per mole of oxygen),

R the universal gas constant and T the absolute temperature, the dissociation pressure for most oxides is low, so oxidation tends to occur in many practical oxidizing media including all but the best vacuum.

Wood and Stott<sup>2</sup> understood that the protection of alloys and coatings at high temperatures often depends upon Cr<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> or occasionally SiO<sub>2</sub> layers. These oxides are nearly stoichiometric and their structures are less known.

During  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> growth, oxygen transport inward down oxide grain boundaries is postulated to predominate over any outward Al<sup>3+</sup> diffusion.

However for  $\text{Cr}_2\text{O}_3$ , outward diffusion of  $\text{Cr}^{3+}$  ions in the oxide grain boundaries apparently predominates, compared with any inward oxygen movement<sup>3</sup>. Inward transport of  $\text{O}_2$  or  $\text{H}_2\text{O}$  is rate-determining for amorphous  $\text{SiO}_2$  growth<sup>4</sup>.

G.Plascencia and T.A.Utigard<sup>5</sup> identified from their experiment on high temperature oxidation mechanism of dilute copper aluminum alloys, the higher the temperatures, the more aluminum is required to achieve good oxidation resistance. While at  $700^\circ\text{C}$ , 2wt% Al is sufficient to decrease oxidation, at  $1000^\circ\text{C}$ , 3wt% Al is required. Based on the rate of oxidation of the alloys tested and their structural features, a kinetic model for alloy oxidation was developed.

Rhines studies<sup>6,7</sup> described the presence of an internal oxidation layer accompanied with an external oxide scale. Spinde<sup>8</sup> only made a qualitative description of his results. He concluded that the oxidation resistance increases as the aluminum content is increased up to 19wt% Al. However, he did not analyze his samples metallographic ally and therefore did not report the presence of any sub-scale.

Y.Niu<sup>9</sup> et.al have analyzed the oxidation of three Ni-6Si-xAl alloys in

1 atm  $\text{O}_2$  at  $1000^\circ\text{C}$  and found that the oxidation of binary Ni-Al alloys containing 6 and 10wt% Al at  $1000^\circ\text{C}$  produces external NiO scales coupled to an internal oxidation of aluminum, while a Ni-Al alloy with 15 wt% Al is able to form external aluminum scales. The addition of 6wt% Si to these Ni-Al alloys prevent in all cases the internal oxidation of aluminum, so that the oxidation behavior of ternary Ni-Si-Al alloys containing 6 and 10wt% Si and Al, to reach the critical value of the volume fraction of internal oxides required for the transition from the internal to the external oxidation of aluminum according to an extension to an extension to ternary alloys according to an extension to ternary alloys of Wagner's criterion for binary alloys.

T.Arima et.al<sup>10-11</sup> have discussed the previous studies on oxidation of Zr metal by dried oxygen gas its kinetics, the nature of oxide films and so on: Fig 2(a to d) shows the results when the mapping analyses by EPMA for the Zr-1Nb and -10Nb samples oxidized at  $600^\circ\text{C}$  for 7 d respectively. The thickness of oxide film of Zr-10Nb is larger than that of Zr-1Nb, which corresponds to the relationships between weight gain and Nb content observed features of oxidized sample are that there are lateral cracks in both oxide films and that Nb atoms do not distribute uniformly in both oxide film and underlying metal but gather in grains.

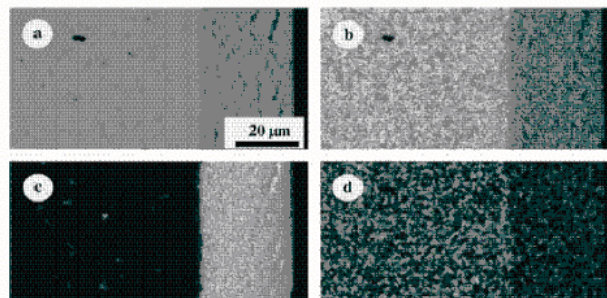


Fig 2(a,b,c and d) mapping analyses by EPMA for Zr-1Nb and -10Nb samples oxidized at  $600^\circ\text{C}$  by T.Arima et.al<sup>10</sup>.

When an oxide layer is developing relatively uniformly in thickness, its growth may be represented by a kinetic law or relationship, typically parabolic or logarithmic for protective behavior. During alloy oxidation, parabolic or logarithmic is often observed.

In practice, many oxidizing alloys are employed where the component is stressed or is susceptible to creep or fatigue<sup>12,13</sup>. The alloy can itself additionally generate its own stresses upon oxidation, which deform it, or cause the alloy or scale itself to fracture.

### Classification of Alloy Oxidation

Components of alloys have different affinities for oxygen and they rarely diffuse at the same rate in the alloy or oxide. Consequently, the simple kinetic rate equation are often not followed and the scale and alloy composition change in a complex way with time.

A minor component may enter and affect the lattice defect structure of the scale, or may accumulate as metal or oxide beneath the main scale. If atomic oxygen diffuses in the alloy precipitation of a less noble metal oxide may occur as internal oxide. As scales often crack, contain voids, spall, sinter or form multiple layers of irregular thickness, hence there is no universal theory for alloy oxidation can exist. Here, Only limiting cases, applicable specifically to binary alloys or more generally to complex practical alloys, quantitative or semi quantitative analysis is possible.

Wood and stott<sup>2</sup> had an opinion that many theoretical papers discuss steady-state scaling where a uniform layers of one particular oxide, possible doped, controls the oxidation rate. Practically this takes time and much scale often forms before this situation is achieved. At this stage factors such as the method of specimen heating, the oxidizing conditions and cold work, grain size, surface finish, and sample thickness and geometry are important in eventual steady-state scale.

### Internal Oxidation and Inter-Granular Penetration

The term internal oxidation is kept for when the oxidation products form as plates, voids, spheres etc., at a reaction front that advances uniformly in to the alloy at a rate independent of structural features such as grain boundaries. Inter-granular oxidation (penetration) occurs when oxidation products develop to greater depths in the vicinity of grain boundaries.

A paper by Wagner<sup>14-17</sup> provides assistance in understanding these observations. When Ni-40Cr is oxidized in 1atm oxygen at 1473K, voids are seen in the alloy to the chromium depletion depth behind the Cr<sub>2</sub>O<sub>3</sub> scale. However, at 1273K, the voids are fewer, tend to be concentrated in the grain boundaries and become, at least partially, filled with oxide. This because the steeper chromium depletion gradient in the substrate permits dissociation of Cr<sub>2</sub>O<sub>3</sub> from the surface, gas transport and then precipitation of Cr<sub>2</sub>O<sub>3</sub> in the voids when the alloy chromium content is higher.

### Stress Generation in Oxide Scales

The formation of an oxide scale on an alloy is accompanied by oxidation induced stresses. In the classical Pilling-Bedworth model, it is suggested that the stresses generated in a growing scale are related to the Pilling-Bedworth ration (PBR) is given by,

$$\text{PBR} = \text{Volume per metal ion in oxide} / \text{Volume per metal in model}$$

This model, which assumes that the oxide form at the scale/metal interface, predicts the sign of growth stresses (compression if PBR > 1, tension if PBR < 1). However, there is no obvious relationship between this ratio and the level of stresses in the scale. Stringer<sup>18</sup> has argued that the volume expansion accompanying oxidation partly accommodated by various mechanisms. Expansion or contraction normal to the oxide/metal interface or high ionic mobility in the interface so that growth stresses are minimised. Srolovitz and Ramanarayanan<sup>19</sup> have calculated the stresses developed in the scale when new oxide along pre-existing grain boundaries. This mechanism has been suggested by Rhines and Wolf<sup>20</sup>.

### Thermal Stresses

Coefficient of thermal expansion of oxides are generally lower than those of high temperature alloys. This mismatch can induce thermal stresses during temperature variations. According to the

residual stress analysis carried out by Evans<sup>21</sup> et al thermal stresses in an oxide layer (thickness t) on a cylindrical substrate (radius a >> t) are

$$\sigma_r = E_{ox} \frac{\Delta\alpha \Delta T}{2(1-\nu_{ox})} (1-1/t) t/a$$

$$\sigma_A = \sigma_z = -E_{ox} \frac{\Delta\alpha \Delta T}{1-\nu_{ox}}$$

Where  $\sigma_r$ ,  $\sigma_A$ , and  $\sigma_z$  are the radial, tangential and longitudinal stresses respectively. E is young's modulus  $\nu$  is Poisson's ratio, r is the distance from the substrate interface,  $\Delta\alpha$  is the difference between the coefficients of thermal expansion ( $\alpha_{ox} - \alpha_{me}$ ),  $\Delta T$  is the temperature range ( $T_{max} - T_{min}$ ) and subscripts ox and me denote oxide and metal respectively. It is interesting to note that no shear stress exists at the surface. A decrease in temperature produces in in-plane compressive stresses at the interfaces. These stresses can be of large magnitude.

### Stress relief

The following mechanisms can relieve the growth and thermal stresses.

#### Plastic deformation of scales

Most oxides do not exhibit significant plasticity at low temperature ( $T < 0.5T_m$ ) because they do not possess the independent slip systems required by Vonmises criterion. However at high temperature ( $T > 0.5T_m$ ) modes of deformation other than dislocation glide can be operative, among which diffusional creep and grain boundary sliding seem the most relevant for the strain rate refers involved during oxidation at high temperatures.

#### Deformation induced in substrate

Stress relief of surface scales may occur by deformation of the substrate as demonstrated by plastic deformation around sharp edges and corners or elongation of their specimens. The plasticity of an alloy can be affected by the compositional change resulting from selective oxidation.

#### Scale buckling, cracking and spallation

Mevrel<sup>22</sup> have made a point that during cyclic oxidation, (under very high stress or very low temperatures) the stresses can be relieved by scale cracking or buckling, depending on the respective scale and scale/metal interfacial strengths. These phenomenon can lead to partial scale spallation and as a result an unprotected substrate area which is aluminum or chromium depleted is exposed to the oxidizing environments.

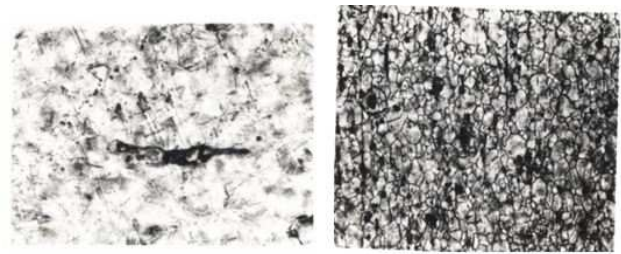
**Present Study and Experimental Work**

The alloy used for the oxidation studies is Inconel 600, a Nickel based super alloy. The chemical composition of the alloy is given in table 1. The specimen was obtained plate form. The specimens were arranged in to 0.5mm thick and cut in to coupons of 20mmx20mmx0.5mm. Electrical muffle furnace was used for this study. The furnace was capable of heating upto 1000<sup>0</sup>c with six Kanthal coils. The power was supplied to the resistors through a controller with an indicator. The temperature fluctuation in the furnace was maintained at plus or minus ±1<sup>0</sup>c.

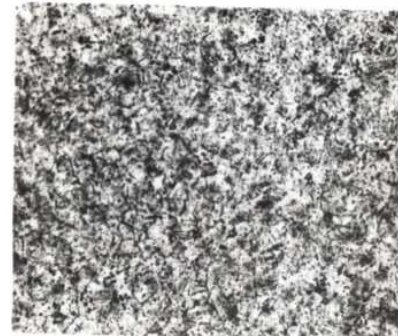
Composition	Weight%
Ni	76
C	0.08
Cr	16
Cu	0.2
Fe	8
Tensile Strength	85,000 lb/in <sup>2</sup>
Yield Point	35,000 lb/in <sup>2</sup>
Elongation	40%

**Table 1.**

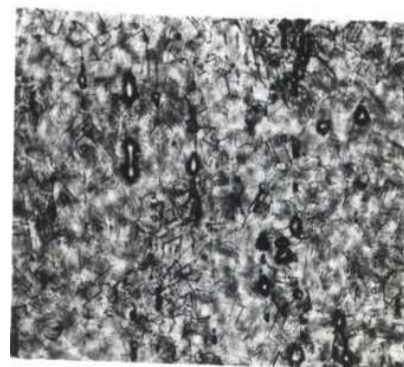
Normal parabolic oxidation was observed at 700 and 750<sup>0</sup>c. But at 750<sup>0</sup>c up to 48 hours slow oxidation occurs and after that the rate of oxidation gradually increases. This may give rise to pseudo like parabolic oxidation. Further observing that with increase in temperature, the weight gain increases. After an exposure of 120 hrs the weight gain varied and shown much variation at 800<sup>0</sup>c. Fig.3 shows that the oxide scales developed on the alloy at different test temperatures. The specimens were subjected to oxidation at 750<sup>0</sup>c for 120 hrs, shown non-protective oxide scales (as shown in fig.4c) metallic regions where the oxide scales have spallen off.



**Fig.3 a) Inconel 600 As received condition Fig 3b) Oxidation of the alloy at 700c for 120 hrs**



**Fig 3c) Oxidation of the alloy at 7500c for 120 hrs**



**Fig 3d) Oxidation of the alloy at 8000c for 120 hrs**

**Temperature: 700<sup>0</sup>C**

**Table: 1.1**

Sl.No	Time (hours)	Initial weight W1 (mg)	Final Weight W2 (mg)	Weight gain (W2-W1) (Mg)	Area (CM <sup>2</sup> )	Weight gain/Area (Mg/CM <sup>2</sup> )
1.0	24	154.33	154.48	0.15	1.77x1.82	0.04656
2.0	48	156.03	156.21	0.182	1.85x1.82	0.0535
3.0	72	155.38	155.58	0.21	1.82x1.82	0.06037
4.0	96	155.84	156.05	0.21	1.81x1.81	0.0641
5.0	120	146.81	147.036	0.2267	1.9x1.80	0.066

Temperature: 750<sup>0</sup>C

Table: 1.2

Sl.No	Time (hours)	Initial weight W1 (mg)	Final Weight W2 (mg)	Weight gain (W2-W1) (Mg)	Area (CM <sup>2</sup> )	Weight gain/Area (Mg/CM <sup>2</sup> )
1.0	24	155.61	156.38	0.77	1.90x1.90	0.20233
2.0	48	151.46	152.25	0.79	1.90x1.90	0.21999
3.0	72	152.05	152.88	0.83	1.90x1.83	0.23871
4.0	96	153.31	154.19	0.88	1.90x1.81	0.25448
5.0	120	149.32	150.36	1.04	1.94x2.02	0.265387

Temperature: 800<sup>0</sup>C

Table: 1.3

Sl.No	Time (hours)	Initial weight W1 (mg)	Final Weight W2 (mg)	Weight gain (W2-W1) (Mg)	Area (CM <sup>2</sup> )	Weight gain/Area (Mg/CM <sup>2</sup> )
1.0	24	153.72	154.15	0.43	1.93x1.82	0.12242
2.0	48	143.44	143.96	0.52	2.10x1.95	0.12698
3.0	72	144.33	144.98	0.65	2.50x1.96	0.13700
4.0	96	156.43	156.98	0.75	2.50x2.00	0.15000
5.0	120	151.71	156.36	0.65	2.0x1.99	0.1633

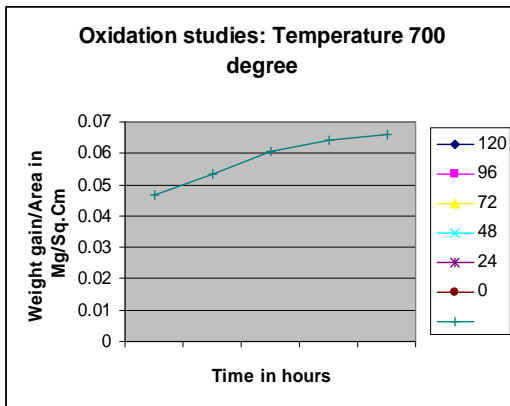


Fig. 4a) Showing pseudo-like parabolic oxidation

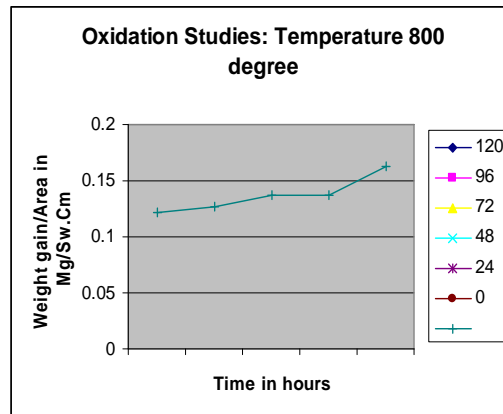


Fig. 4 c) showing parabolic rate law and arrhenous relationship with parameters(also shows linear relationship at larger exposure time)

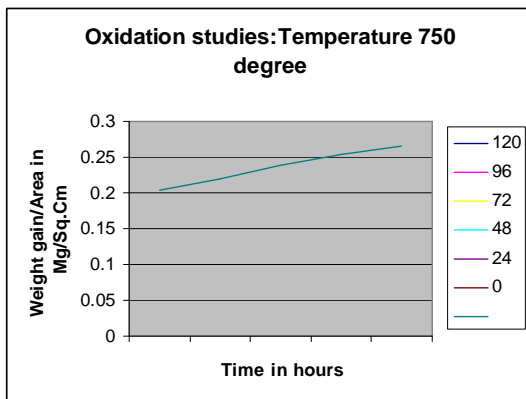


Fig. 4 b) Showing parabolic rate law and arrhenous relationship with parameters

**Conclusion**

Under purely oxidizing conditions the alloy showed parabolic kinetics. The weight gain increases with increases with increase in temperature. The oxide scales developed on the alloy under purely oxidizing condition were fairly adherent except at a test temperature of 750<sup>0</sup>c, where oxide spalling was observed in few regions. Internal oxidation in the form of pits in big sizes and depth were observed at the highest test temperature 800<sup>0</sup>c. The parabolic law is considered as:  $w^2 = k_p t + c$

where w is the weight gain per area,  $k_p$  is the parabolic rate constant or ionic diffusion rate constant and t is the time. The value of  $k_p$  determines the nature of oxide scale. Rate determining step in this

oxidation process is the diffusion of ions in to the oxides. Here the ionic diffusion controlled oxidation was observed. This is a characteristic of unsteady state diffusion.

#### **Oxidation models**

The oxidation model may be obtained by using the Fics second law as follows:

$J_{ions} \propto 1/\Delta x$  where  $\Delta x$  is the thickness of the scale. The changes in thickness is characterized by change in flux (diffusion). The thickness of oxide scale = weight gain /  $A \times \rho$  wher  $A$  is the area of the specimen and  $\rho$  is its density. The rate of change of thickness of the scale can be found as  $dx/dt = k(\text{concentration})^8$  where  $x$  is the thickness and  $t$  is the time.

In this present study the alloy oxidation obeyed parabolic law and it resulted thick coherent oxide scales.

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#### **References**

- [1] T.I.BARRY,A.T.DINSDALE:'Thermodynamics of metal-gas-liquid reactions' Materials Science and Technology- 1987 vol 3.501-508.
- [2] WOOD and STOTT:'Oxidation of alloys' Materials Science and Technology- July 1987 vol3. 519-530
- [3] ATKINSON,Report AERE-R-11293,Atomic Energy Research Establishment,Harwell,1984
- [4] N.F.MOTT,Philos,mag,1982,45A,323-329
- [5] G.PLASCENCIA,T.A.UTIGARD;Corrosion Science 47,(2005),1149-1163
- [6] F.N.RHINES,Trans.Am.Inst.Mining Metall.Engg,1327(=,(1940),246-290
- [7] F.N.RHINES,W.A.JOHNSON,W.A.ANDERSON,Trans.Am.Inst.Mining Metall.Engg,147,(1942),205-221
- [8] P.SPINDE,La.Metall.Ital,12,(1953),457-461
- [9] Y.NIU etal,Corrosion Science 48,(2006)1-22
- [10] T.ARIMA et.al.J.Nucl.Mater.,257(1998)67
- [11] G.HAN,W.D.CHO,Materials and EnggA,419,(2006)76-85
- [12] T.SMITH,J.Electrochem,112,(1965),39
- [13] S.NOMURA,C.AKUTSU,Electrochem.Tech,4,(1966)39
- [14] C.WAGNER:Journal of Electrochemical Society:1956,103,571-580.
- [15] C.WAGNER:Journal of Electrochemical Society:1956,103,627-633.
- [16] C.WAGNER:Journal of Electrochemical Society:1959,63,771-779.
- [17] C.WAGNER: Corrosion Science,1968,8,889-893.
- [18] J.STRINGER: Corrosion Science,1970,10,518-543
- [19] D.J.SROLOVITZ and T.A.RAMANARAYANAN: Oxidation of metals,1984,22(3/4),133-146
- [20] F.N.RHINES and J.J.WOLF:Metallurgical transactions,1970,1,1701-1710.
- [21] A.G.EVANS,G.B.CRUMLEY and R.E.DEMARAY:Oxidation of metals,1983,20(5/6),193-216.
- [22] R.MERVEL: Materials Science and Technology 1987,7,vol3,531-535.
- [23] O.KUBASCHEWSHI and B.E.HOPKINS:'Oxidation of metals and alloys';(2nd edn),1967,London,Butterworths.
- [24] J.STRINGER: Keynote address,'High temperature corrosion of super alloys' Materials Science and Technology, July 1987,vol 3.