

## Isothermal Oxidation of Simple and Pt-Modified Diffusion Coating on Inconel Alloy 600 In Water Vapor

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### Abstract

In this work the oxidation behavior of both inconel alloy 600 and coated system (Pt-modified aluminide coating) was investigated in pure water vapor  $H_2O$  in the temperature range 700 - 900 °C. The platinum was deposited by electrochemical method. Pt-modified aluminide coating was applied to inconel alloy 600 by using single-step high activity pack cementation method. The weight gain measurements indicate that the oxidation kinetic is parabolic for uncoated and coated alloy. At temperatures below 900 °C the inconel alloy 600 is less aggravated in water vapor environments because it is a chromia former alloy. At 700 °C, water vapor does not have a significant effect on the spalling of oxide scales. At 900 °C, water vapor causes spalling of the oxide scales during isothermal oxidation of inconel alloy 600. Therefore, it is concluded that this alloy should not be used above 900 °C in water vapor environments. Large voids were found at the oxide scales-substrate interface and at grains or at grain boundaries due to the chromium outward diffusion toward the oxide scales.

At 900 °C, the parabolic rate constant ( $k_p$ ) of the coated system was one order of magnitude lower than that for the uncoated alloy. It was concluded that, water vapor exhibit little effect on the Pt-modified aluminide coating. Oxide phases that formed on coated system are:  $Al_2O_3$ ,  $NiAl_2O_4$ ,  $Cr_2O_3$ , and  $NiFe_2O_4$ .

**Keywords:** Oxidation, pack cementation, super alloy, coating, inconel alloy.

اكسدة سبائك الانكونيل – بلاتينيوم – الالمنيوم تحت ظروف بخار الماء

الخلاصة

تم دراسة سلوك الأكسدة للسبائك الفائقة Superalloys (سبيكة انكونيل 600 inconel) ذات الأساس من النيكل Ni بالإضافة الى سلوك التأكسد لنظام الطلاء Coating System المؤلف من سبيكة الانكونيل 600 كأساس substrate وطبقة من البلاتين Pt-Layer تم ترسيبها بتقنية الطلاء الكهروكيميائي Electrochemical ثم عوملت بالانتشار الحراري ليتم أخيراً ترسيب الألومنيوم عليها باستخدام تقنية الطلاء بالسمنتة Pack Cementation Technique. تم دراسة سلوك الأكسدة للأنظمة أعلاه في وسط و بخار الماء  $H_2O$ ، عند درجات حرارة هي 700-900 م°. تشير نتائج الدراسة الحالية الى أن السلوك الكيناتيكي العام للتأكسد لسبيكة الانكونيل 600 (الغير المطلية والمطلية) يتبع تقريباً قانون القطع المكافئ  $k_p$  Parabolic. عند درجة حرارة 700 م°، وجد أن بخار الماء ليس له تأثير يذكر على تنشيطية الأكاسيد. عند درجة حرارة 900 م° يشير ذلك الى صعوبة استخدام هذه السبيكة في هذه الأوساط في درجة حرارة أعلى من 900 م°.

أن قيمة ثابت معدل التأكسد  $k_p$  عند درجة حرارة 900 م° للسبيكة المطلية اقل بمرتبة عشرية واحدة من قيمة ثابت معدل التأكسد  $k_p$  للسبيكة غير المطلية. تشير النتائج الى تكون فجوات كبيرة عند طبقة الأوكسيد/ الارضية وذلك بسبب عملية الانتشار لعناصر السبيكة كالكروم. تشير نتائج التحليل بالأشعة السينية للسبيكة المطلية ظهور أكاسيد الكروم و النيكل إضافة الى أكسيد الألومنيوم كما يلي

$NiAl_2O_4, Cr_2O_3, Al_2O_3, NiFe_2O_4$ .

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## Introduction

High-temperature degradation of alloys in water vapor turns out to be more complex than anticipated, not only because H<sub>2</sub>O favors the evaporation of Cr via CrO<sub>2</sub> (OH) and refractory-metal oxide, but also because H<sub>2</sub>O can form H<sup>+</sup> and (OH)<sup>-</sup> ions within an oxide scale, thus influencing their diffusivity and stoichiometry. Water vapor also promotes decarburization of alloys, which may lead to compositional changes in the alloy, affecting the mechanical properties of alloys. The various effects of water vapor on oxide scales and their parent substrates are so far not fully understood [1].

A number of mechanisms have been proposed to explain the destruction of the protective chromia scale by the presence of water vapor. These are: (1) Formation of volatile Cr-oxihydroxides or (2) Fe-hydroxides, (3) enhanced surface reaction kinetics, (4) defects in the oxide lattice and (5) formation of oxygen bridges by H<sub>2</sub>O/H<sub>2</sub>-mixtures in oxide pores [2].

Hussain and others [3] studied the oxidation behavior of incoloy 825 in steam between 600 - 1000 °C". They found that at 600 °C, the initial oxidation rate is somewhat slower than that for longer duration, but overall the

reaction can be described as cubic. At 900 and 1000 °C, a roughly cubic rate law governed the reaction kinetics for 24 and 6 hr of exposure, respectively, where a transition in kinetics toward a parabolic rate law was observed.

## Materials And Methods

The spectrochemical analysis of Ni based superalloy ( inconel alloy 600) used in this study was carried out at (Physics Department- College of Science – Baghdad university) as shown in table 1 and the nominal composition of this alloy as chemical limits is shown in table 2.

Coupons of dimensions 2 cm × 2 cm × 0.4 cm were cut out from inconel 600 sheet. Small hole 1 mm in diameter was drilled in each coupon for holding. All the surfaces were wet ground using 150, 300 and 600 grit silicon carbide papers. Pt-modified aluminide coating was produced on inconel alloy 600 substrates first by electrochemical coating with platinum layer followed by diffusion annealing at 850 °C for up to 0.5 hours and consequently increased temperature to 1034 °C for up to 2 hours in a vacuum furnace at 10<sup>-3</sup> Torr. Electrodeposited Pt layer coatings are formed by electroplating technique on Ni-based alloy samples . A platinum plating system was set up which

includes a polyvinylidene fluoride (PVDF) plating tank (35 x 25 x 25) cm, a Teflon immersion heater, a DC power source, and the anode and cathode bars. Samples of inconel alloy 600 were plated using Pt20-Q salt ( $[\text{Pt}(\text{NH}_3)_4]\text{HPO}_4$  from Johnson Matthey Catalysts) electrolyte at 90-95°C with Pt concentration greater than 10 g/l. The Pt thickness was ~2.5  $\mu\text{m}$  after 15 min of plating time based on the mass gain.

Subsequently, the diffusion treated specimens were pack aluminized to produce a platinum modified aluminide coating using single-step high-activity above pack cementation method. The pack used for aluminizing consisted of 10 wt. % Al powder (50 to 150  $\mu\text{m}$  in particle size) as an aluminum source, 2 wt. %  $\text{NH}_4\text{Cl}$  as the activator, and the balance was 88 wt.% of  $\alpha$ -alumina (70-210  $\mu\text{m}$ ) as the inert filler. The aluminizing process was carried out at  $1034 \pm 5$  °C for up to 4 hours inside a closed tube furnace. After the aluminizing treatment, the specimens were cleaned and weighed to determine the aluminum pickup. No, further heat treatment was given to the specimens after aluminizing [5].

#### Oxidation in Water Vapor

The experimental setup for oxidation in water vapor includes vertical tube

furnace, evaporator, microbalance, and steam lines as shown in Fig. 1. The oxidation test in water vapor were conducted in the temperature range of 700 - 900 °C, and the exposure time up to 50 hrs under atmospheric pressure for inconel alloy 600 (uncoated) and for platinum aluminide coating (coated system). Weight gain was monitored and recorded in the work sheet at suitable intervals. The samples were then examined by the optical microscopy and SEM (FEI/Philips/XL-30 W/TMP). The phases present in the alloys were identified with X-ray with General electric diffractometer, operating at scanning speed of 2° (2 $\theta$ ) per minute with  $\text{Cu K}\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ).

#### Results And Discussion

##### Oxidation of Inconel alloy 600(uncoated)

The oxidation behavior of inconel alloy 600(uncoated) in water vapor was studied at temperatures between 700 °C and 900 °C for 50 hours. From Fig. 2 a computer program is used to calculate the best fit to the equation ( $\Delta W/A = k_p t^n$ ). Where,  $\Delta W/A$  is the weight gain per unit area,  $k_p$  and  $n$  are constants and  $t$  is the oxidation time. Values of  $n$  are shown in Table 3. The value of  $n \approx 0.5$  indicates that the oxidation rate of inconel alloy 600 in

the temperature range of 700-900 °C is parabolic and the oxidation is controlled by diffusion mechanism [6]. The value of activation energy ( $Q$  in kJ/mole ) was calculated from Plot of  $k_p$  vs  $1/T$  for isothermal oxidation .

In general, the results of this study show that water vapor affects greatly the oxidation behavior of the inconel alloy 600 at the temperature range (700 to 900 °C). The increase in weight gains in water vapor compared with air is due to the lack of selective oxidation of chromium in this chromia -former alloy.

X-ray diffraction patterns for the specimens oxidized in water vapor at temperatures 700 to 900 °C for up to 50 hour are identified the surface oxide phases. The surface oxides were identified as  $Cr_2O_3$ , as major components attributed to the selective oxidation of chromium under the isothermal oxidation in water vapor. Also, the other phases mentioned mainly involved are NiO, and a complex spinel phases  $Ni(Cr, Fe)_2O_4$ .

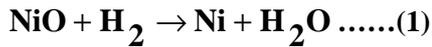
The surface oxides formed is shown in Fig. 3, which illustrate that, the contribution of the oxides formed at triple point of grain boundaries and the formation of large nodules.

Chromium grain boundaries diffusion (short circuits path) in the alloy substrate plays an important role in the

formation of protective  $Cr_2O_3$  in the external layer or beneath it as sub-layers corresponding to the concentration of Cr in the base alloy. A continuous layer of chromia forms at the grain boundaries while a continuous layer of nickel oxide forms on the grain surface. While the NiO layer is growing, the sub-layer of  $Cr_2O_3$  becomes continuous by lateral growth due to the diffusion of Cr from the grain boundaries to the center of the grains. When the chromia sub-layer is continuous, the NiO layer stops growing and the oxidation kinetics only reflect the growth of the  $Cr_2O_3$  layer [7].

Chromium outward transport was responsible for the growth of the external sub-scale, leading to void formation at its internal interface. The growth of internal sub-scale, is more rapid in  $H_2O$  than in air, was due to the transport of oxygen-containing species, slow-diffusing oxide ions and probably very mobile hydroxide ions in  $H_2O$ .

The growth mechanism of these scales is the dissociation mechanism explained as: the reaction of water vapor to form NiO at the external surface yields hydrogen part of which is assumed to diffuse inward to form water vapor within voids by reaction and decomposition of NiO as:



The generated water vapor in the voids of inner scale acts as a carrier gas for oxygen leading to oxide formation at the scale/alloy interface, internal oxides and hydrogen which back diffuses to react with oxide at outer void surface. When oxidation starts, Ni, Fe, and Cr oxidize simultaneously to form nickel, iron, and chromium oxides. Ni oxide reacts to form spinel phase  $\text{NiCr}_2\text{O}_4$ . The oxidation rate is slow because the  $\text{NiCr}_2\text{O}_4$  scale serves as a barrier against oxygen inward diffusion and outward metal ions diffusion.

In water vapor environment, Ni oxidation is slower than that in oxygen and the rate changes from parabolic to linear [8,9]. This is believed to result from the difficulty in forming adsorbed oxygen atoms on the surface of NiO, so that the adsorbed species are mainly hydroxyl ions  $\text{OH}^-$  which could not enter the scale of P-types oxide. Therefore, the rate controlling steps becomes the surface reaction to provide oxygen atoms from the adsorbed  $\text{OH}^-$  to react with the Ni cations arriving at the scale gas interface. It is also possible that hydrogen ion transport down NiO grain boundaries may cause the scale growth to be increased which would increase the concentration of

cation vacancies and hence the outward flux of Ni. In water vapor, Cr oxidizes faster and rapid growth results. This result is of importance, as it seems that the catastrophic oxidation in the presence of water vapor of chromia forming alloys is induced by oxygen and hydrogen penetration within the protective scale and reaction at the metal-oxide interface forms a large amount of (Ni, or Fe)-chromium spinel. Water vapor is known to accelerate the oxidation rate of chromia forming alloys, which would normally be very corrosion resistance at similar temperature in dry air. Fig. 4 illustrates the oxide layers growth on inconel alloy 600 in water vapor. It has been many hypothesized that the addition of water vapor results in increased porosity or defects in the scales.

The values of  $k_p$  for the uncoated inconel system obtained between 700 to 900 °C in water vapor are shown in Table 3 . It is clear that the oxidation kinetics is parabolic. The  $k_p$  value at 900 °C is four times the  $k_p$  value at 700 °C. The values of  $k_p$  for the uncoated inconel system at 900 °C in  $\text{CO}_2$  [11] and in water vapor environment [present work] are approximately equal ,but one order of magnitude larger than that obtained in air [ 10 ].

### Oxidation of Coated System:

The isothermal oxidation of Pt – modified aluminide coating were performed in water vapor at 800 and 900 °C. The weight gain of the specimens during oxidation is plotted as a function of time in Log-Log scales as shown in Fig. 5.

The values of  $n$  and  $k_p$  were calculated in the same manner as before and the kinetic behavior of oxidation of coated system in water vapor at temperatures of 800 and 900 °C follows the parabolic rate over the entire 50 hours as shown in Table 4. The  $k_p$  value obtained at 900 °C in water vapor is  $k_p = 2.94 \times 10^{-5}$  for the coated system and about one order of magnitude lower than that for the uncoated inconel alloy 600  $k_p = 2.1 \times 10^{-4} \text{ mg}^2/\text{cm}^4 \cdot \text{s}$ . On the other hand, at 900 °C the  $k_p$  value obtained in air [10] and in CO<sub>2</sub> [11] environments showed similar oxidation behavior. But the  $k_p$  value in water vapor is 30 times the  $k_p$  value in air as shown in Table 4.

At 800°C and 900 °C, the Pt- modified aluminide coatings increase the oxidation resistance in water vapor. At these temperatures water vapor (H<sub>2</sub>O) yield higher oxidation rates than that obtained in air, but the effect is small at 800 °C where good oxidation resistance is found. The effect of H<sub>2</sub>O in its vapor state on the oxidation rate was found to

be particularly large because the scales contain appreciable amounts of porosity and voids. This strongly suggests that gaseous transport across voids with (CO<sub>2</sub>, CO, and O<sub>2</sub>) and (H<sub>2</sub>O, H<sub>2</sub>, and O<sub>2</sub>) in CO<sub>2</sub> gas and water vapor environments respectively as carrier gas [5].

In general, the values of  $k_p$  indicates that the modification of aluminide coating with platinum on inconel alloy 600 results in a significant improvement in the oxidation resistance. The changes that take place in phase constitution of coated system during the isothermal oxidation in water vapor have been less lightening because of the complexity of such systems and need high accurate facilities. It can be stated that the various stages involved in the degradation process has attempted by evaluation of the various stages of micro-structural degradation during oxidation of a high activity platinum-modified aluminide coating on inconel alloy 600.

Isothermal oxidation of coated system is shown less affected by the water vapor environment used in this investigation; the development of continuous adherence alumina scales is inhibited in water vapor conditions, more extensive transient oxidation prior to continuous alumina layer takes place

compared to oxidation in air. The growth of  $\text{Al}_2\text{O}_3$  scales is significantly slower than  $\text{Cr}_2\text{O}_3$  scales and alumina does not have a volatility problem like chromia scales, so that catastrophic problems appear less likely for this case.

### Conclusions

1- The isothermal oxidation kinetics of Inconel alloy 600 in the water vapor between 700- 900 °C is parabolic. At 700 °C, the water vapor effects may be very small and the only effect at this temperature is in the selective oxidation.

The main major oxide scales phases that are present here are  $\text{Cr}_2\text{O}_3$ , and spinel phases like  $\text{NiCr}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$ .

2- The Inconel alloy 600 coated system exhibits good oxidation resistance in water vapor compared with the uncoated alloy at the same identified conditions and the oxidation kinetics is parabolic .

3- Alumina oxide scale is not the only phase on the surface of components; other phases are obtained such as  $\text{NiAl}_2\text{O}_4$  and others.

### Acknowledgement

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**Table (1) Spectrochemical analysis of inconel alloy 600.**

|              |             |             |              |            |            |            |             |            |              |            |            |
|--------------|-------------|-------------|--------------|------------|------------|------------|-------------|------------|--------------|------------|------------|
| <b>El.</b>   | <b>Ni</b>   | <b>Cr</b>   | <b>Cu</b>    | <b>Fe</b>  | <b>Mn</b>  | <b>Si</b>  | <b>S</b>    | <b>C</b>   | <b>Al</b>    | <b>Mg</b>  | <b>Mo</b>  |
| <b>Wt. %</b> | <b>Rem.</b> | <b>19.0</b> | <b>0.099</b> | <b>8.4</b> | <b>0.1</b> | <b>0.2</b> | <b>0.01</b> | <b>0.1</b> | <b>0.399</b> | <b>0.1</b> | <b>0.5</b> |

**Table (2) Nominal composition of inconel alloy 600 according to [4].**

| Chemical Limits |      |      |     |      |      |       |       |       |
|-----------------|------|------|-----|------|------|-------|-------|-------|
| Ni              | Cr   | Cu   | Fe  | Mn   | Si   | S     | P     | C     |
| 72.0            | 15.5 | 0.5  | 8.0 | 1.0  | 0.5  | 0.015 | 0.015 | 0.065 |
| Min.            |      | Max. |     | Max. | Max. | Max.  | Max.  |       |

**Table (3)  $n$  values & parabolic oxidation rate constants  $k_p$  for oxidation of uncoated inconel alloy 600 in H<sub>2</sub>O for up to 50 hour.**

| Temperature, °C | $n$ , value | $k_p$ , (mg <sup>2</sup> /cm <sup>4</sup> .s) |
|-----------------|-------------|---|
| 700             | 0.55        | $5.2 * 10^{-5}$                               |
| 800             | 0.51        | $1.3 * 10^{-4}$                               |
| 900             | 0.45        | $2.1 * 10^{-4}$                               |

**Table (4)  $n$  values & parabolic oxidation rate coefficients  $k_p$  for oxidation of coated system in three different environments.**

| Environment                   | 800 °C                                      |      | 900 °C                                      |      |
|-------------------------------|---|------|---|------|
|                               | $k_p$ (mg <sup>2</sup> /cm <sup>4</sup> .s) | $n$  | $k_p$ (mg <sup>2</sup> /cm <sup>4</sup> .s) | $n$  |
| Air [Ref. 10]                 | $3.08 * 10^{-7}$                            | 0.56 | $6.63 * 10^{-7}$                            | 0.44 |
| CO <sub>2</sub> gas [Ref. 11] | $2.7 * 10^{-5}$                             | 0.55 | $6.2 * 10^{-5}$                             | 0.61 |
| Water vapor<br>[Present work] | $8.83 * 10^{-6}$                            | 0.5  | $2.94 * 10^{-5}$                            | 0.45 |

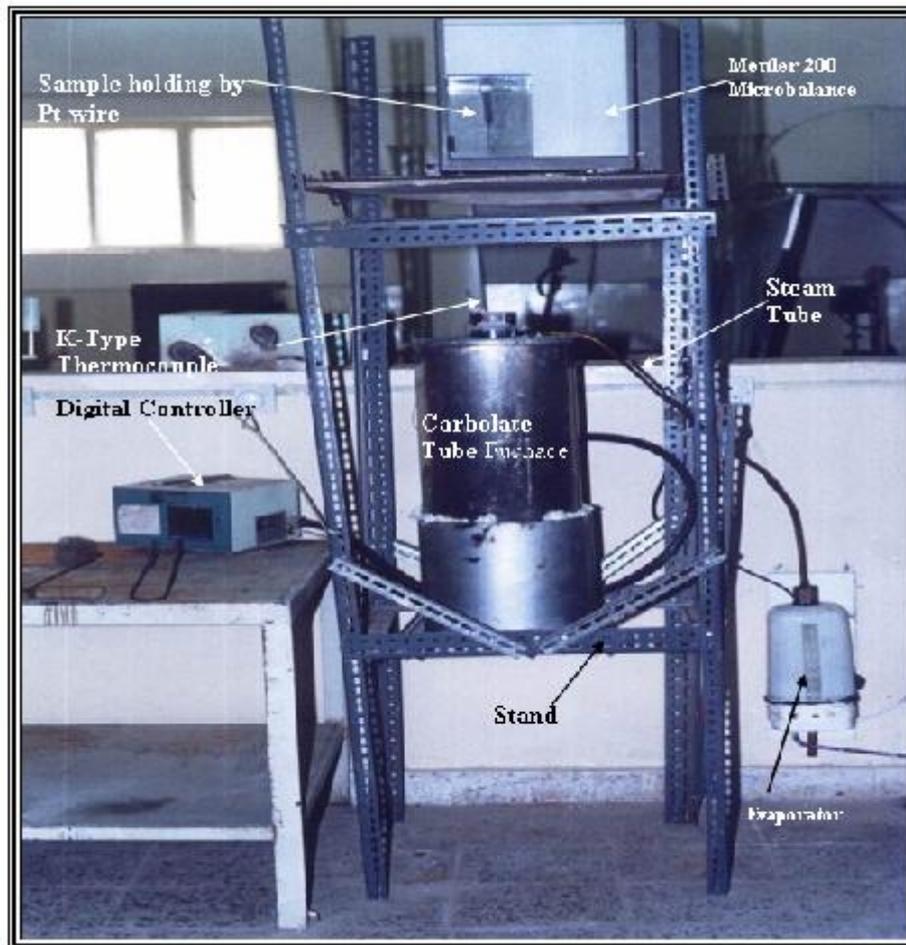
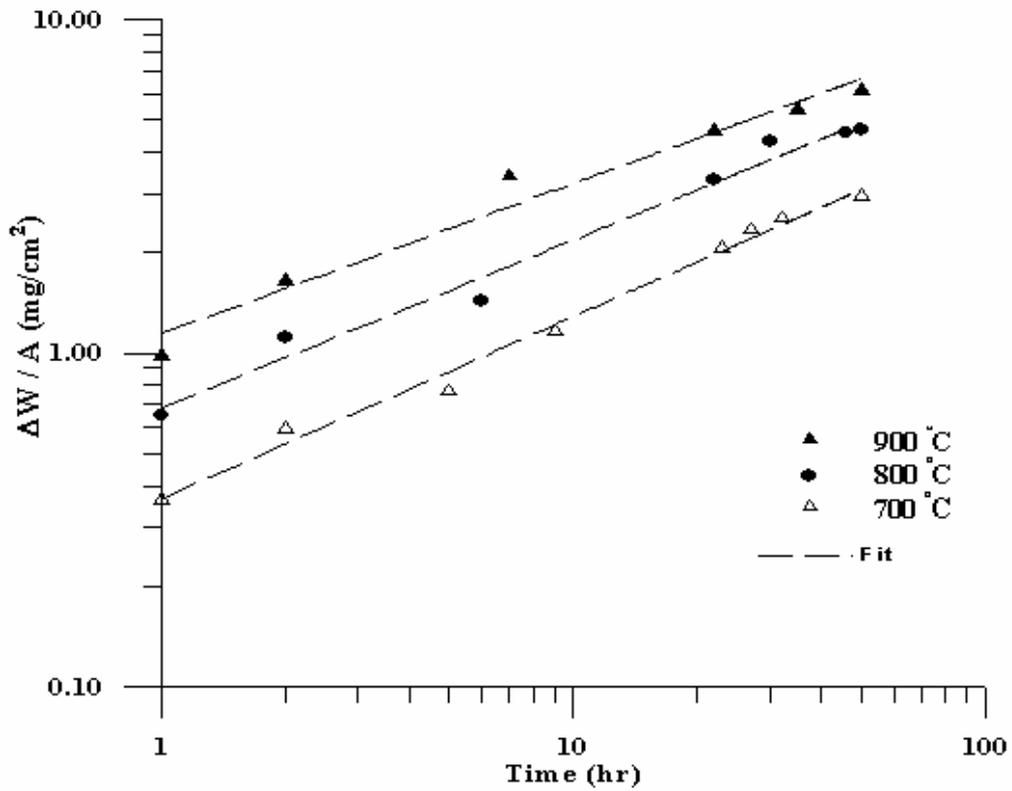
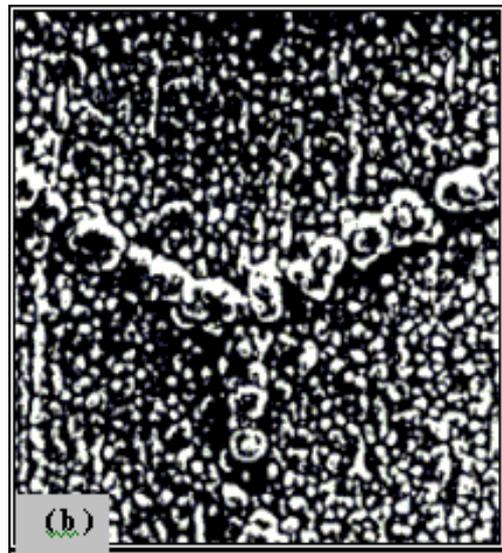


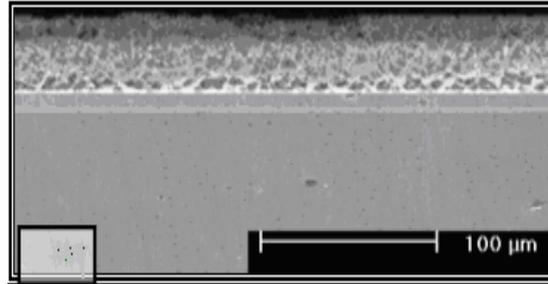
Figure (1) Apparatus used for high temperature oxidation tests in water vapor  $H_2O$ .



Figure(2) log-log plots of oxidation weight-gain data for inconel alloy 600 oxidized in water vapor at700-900 °C for 50 hrs.



Figure(3) Top view micrographs of inconel alloy 600 oxidized in water vapor for up to 50 hour at 800 °C.



Figure(4) Cross-section of SEM for oxide scale growth on inconel alloy 600 oxidized in water vapor for up to 50 hr at 800 °C.

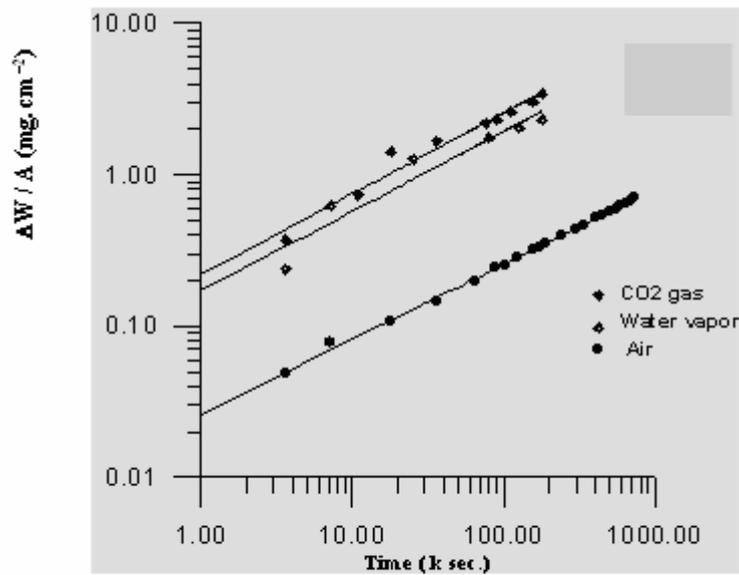


Fig 5 log-log plots of oxidation weight-gain data for coated system oxidized in three different environments at: 900 °C.