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Improvement of Oxidation Resistance of Inconel 600 Alloy by Pack Cementation Process

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Abstract

The aim of this paper is to improve the oxidation resistance of Inconel 600 alloy by diffusion coating. In this study, (Si and Al) and (Al, Si and Y_2O_3) were simultaneously deposited by cementation process into Inconel 600 alloy at 1120°C for the different times (2,4,6,8) hours. The pack powder mixture consists of 18Al-8Si-2NH$_4$Cl-72Al$_2$O$_3$ (wt.%) for silicon modified aluminide diffusion coating and replaced 1% from Al$_2$O$_3$ by Y_2O_3 for yttria doped silicon modified aluminide diffusion coating. Cyclic oxidation was carried out at 50 hours at 900°C, 5 hours for each cycle. The results showed that the coatings microstructure consists of two layers: outer layer and inter-diffusion zone. The best oxidation resistance was found for the deposition by yttria-doped silicon modified aluminide diffusion coating from 6-8 hours of coating time. The phases formed after cyclic oxidation for both coated type and uncoated of Inconel 600 alloy are Ni, NiO, NiFe$_2$O$_4$, (Cr,Fe)$_2$O$_3$, AlNi, CrO$_3$, α-Al$_2$O$_3$, and Y$_4$Al$_2$O$_9$.

Keywords: Oxidation resistance; Inconel 600 alloy; Cementation process

Introduction

Ni-based single crystal super alloys have been widely used in the industrial gas turbines and jet engines. The materials with superior properties, such as mechanical strength and oxidation resistance are required for high temperature applications. Recently, the surface operating temperatures of gas-turbine blades could reach 1200°C or even higher. Aircraft engines represent a demanding area for advanced materials and coatings. In the turbine section, nickel alloys are used which have to be protected against the effects of the operating temperatures. Therefore, rotating and stationary parts (i.e. blades and vanes) in this area are often diffusion coated because this process offers high protection at relatively low cost. Diffused coatings are used to protect the nickel-based super alloys at high temperatures, which are dependent on NiAl. It is usually produced by the cementation process. The process of the cementation activated by halide salts is the process of deposition of chemical vapours in a localized controlled location [1,2]. The process is low cost and especially suitable for the production of uniform and smooth formation of the coating diffusion of the desired thickness on the structural alloy components of complex shapes and different sizes. Thereby, oxidation resistant metals, like aluminium, chromium and silicon are enriched on the surface. These metals form protective oxides during operation and extend the life-time of the turbine part considerably [3]. Therefore, one of the important requirements for a protective oxide scale to provide high-temperature oxidation resistance is the scale adherence to the substrate. Addition of oxygen-active elements (OAE) is found to improve the adherence of Al$_2$O$_3$ scales. The objective of this paper is to find the favourable conditions of the oxidation resistance by diffusion coating process [4].

Experimental Work

The nickel-based high-temperature IN 600 alloy with a nominal alloy composition of Ni-15.35Cr-8.32Fe-0.342Mo-0.0254Si-0.175Mn-0.025Cu-0.168Al-0.181Ti-0.074C-0.032V-0.073Co-0.014P was used as a substrate. Rectangular specimens with the dimension of 15.0×15.0×3.0 mm were ground by emery paper and polished, then washed by ultrasound washing machine. After that, the specimens were co-deposited with Al-Si and Al-Si-Y$_2$O$_3$ by pack cementation process. In a normal pack cementation process,

the substrates to be coated are embedded in a sealed or semi-sealed container together with a well-mixed pack powder containing the deposition elements, halide activator and inert filler. The pack powder mixture consists of 18Al-8Si-2NH$_4$Cl-72Al$_2$O$_3$ (wt. %) for silicon modified aluminide diffusion coating and replacer 1% from Al$_2$O$_3$ by Y$_2$O$_3$ for yttria doped silicon modified aluminide diffusion coating. The pack process was carried out at 1120°C for different times (2,4,6,8) hours under argon atmosphere. The NH$_4$Cl was dried in an oven at 90°C for 24-hr before mixing with other powders. The pack powder was mixed in a ball mill at 300 rpm for 180 min. with the addition of normal-hexane (n-C$_6$H$_{14}$) in order to prevent the powders oxidation due to frictional heat [5]. The pack was then dried at 75°C for 10 hours.

The oxidation test was conducted in static air in a furnace at 900°C for 50 hours, 5hours for each cycle. The specimens were taken out of the furnace to cool at room temperature for a weight measurement and then backed to the furnace to continue the oxidation test. The mass gain of these specimens was measured by a precision analytical balance. Three measurements for weight gain at each time were taken and the average value was employed (Figure 1).

Result and Discussion

Coating microstructure

The cross-section of the coating layers of the samples after (2,4,6,8) hours for two types of the coating, consist of the outer layer and inter-diffusion zone. The main thicknesses of coating layer are 132, 170, 225, 234 and 93, 126, 144 and 153 for two types of coating, respectively. XRD analysis results showed that the different phases formed are Ni$_2$Al$_3$, Fe$_3$Si, Ni$_3$Si$_2$, Al1.1Ni0.9, Ni$_2$Si, AlNi and YNi$_{10}$Si$_2$. When

nickel diffuses outwardly, its concentration in substrate reduces. This results in the precipitation of the dissolved substrate heavy elements in the form of columns. In the coating sub-layer of all four coatings, specimens containing some refractory precipitate can be observed, these precipitates, forming mainly during the pack cementation process as shown in Figure 2, depend on composition of the base metal. Therefore, these precipitates can be formed by rejection of the heavy elements from this compact structure, within which the bright precipitates can be observed. This sub-layer is rich in Al and poor in Ni comes from the substrate. Figure 2 indicates that the distribution, size and amount of precipitates within the coatings sub-layer changed substantially after different times of deposition. Most of these precipitates were decomposed when the outer layer was transformed from Ni_2Al_3 to Ni rich NiAl.

Cyclic oxidation of IN 600

Cyclic oxidation of uncoated IN 600: Oxidation kinetics studies provide valuable information about the oxidation mechanism, and the step of limiting the total rate of the reactive oxidation rate measurements is usually used as a basis for quantitative description of oxidation behavior.

Changes in weights were recorded to determine the kinetic mobility in dry air at 900°C for up to 50 hours in 5 hours cycle. Specific weight change data from the IN 600 alloy are drawn for this test in Figure 3. As a function of time. Primary motility is rapid, but the specific weight-change rate gradually decreases in longer times. Kinetics can be described by examining the fixed time growth rate or the value of n, which is found by the following equation [6,7]:

$$\Delta W/A = ktn$$

Where, ΔW is the weight change, A is the sample surface area, k is the oxidation rate constant, n is the growth- rate time constant, and t is the time of oxidation.

From Figure 3, n-value at 900°C is calculated from a computer program according to the best fit to equation. At 900°C, the n-values are (0.55). It is found that the relationship is parabolic when n=0.5, the exponential constant n characterizes the oxidation rate as follows: if n=1, the oxidation rate is linear; n=0.5, the oxidation is theoretically parabolic; and if n=0.33, then the oxidation rate is cubic. When the value of n is greater or lower than 0.5, then the oxidation kinetic does not fall in the simple parabolic behavior and this implies a faster or slower oxidation rate. For example, for n>0.5, it is an over parabolic, while for n>0.5, the rate is under parabolic (sub-parabolic), the results show that the sub-parabolic may be found because the of grain boundary (short circuits) mechanisms. Deviation from the theoretical value of n=0.5 can be explained by an oxide layer cracking to a sudden increase in the surface area in contact with oxygen and then accelerating the oxidation kinetics. For the parabolic kinetics, the rate equation takes the form: $\mathbf{\Delta W/A = kt^{0.5}}$

Where, k now refers to the parabolic rate constant. A plot of weight change vs. square root of time gives a line; the slope is the parabolic rate constant in units of $(mg/cm^2)/h^{1/2}$, as shown in Figure 4. The kp value is then squared to give kp in units of $(mg^2/cm^4)/h$, as in the following expression: $(W/A)^2 = Kpt$.

The point to be noted also is that the other values of n and kp in this study are calculated with the same procedure explained above.

Figure 5 depicts the (LOM) microstructure of the cross section and top view of the uncoated IN 600 samples after exposed to cyclic oxidation in air at 900°C for 50 hours each cycle 5 hours.
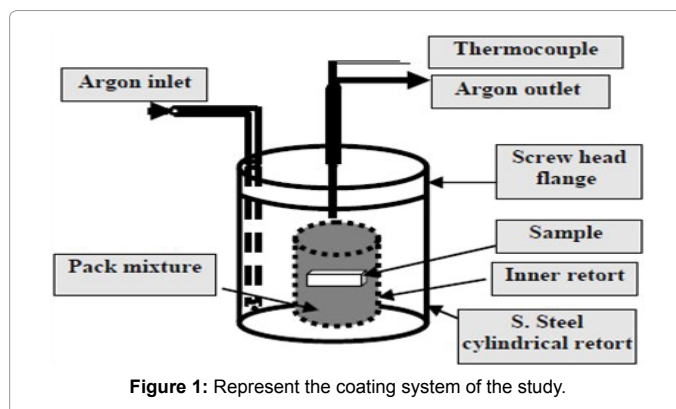

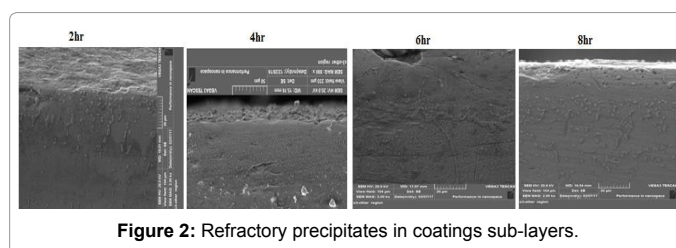**Figure 1:** Represent the coating system of the study.

Figure 2: Refractory precipitates in coatings sub-layers.
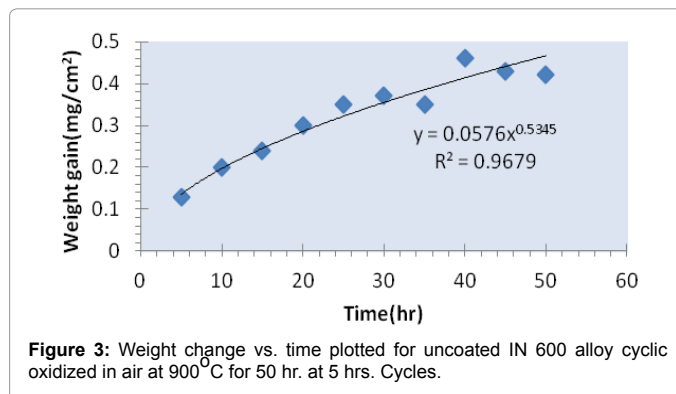

Figure 3: Weight change vs. time plotted for uncoated IN 600 alloy cyclic oxidized in air at 900°C for 50 hr. at 5 hrs. Cycles.
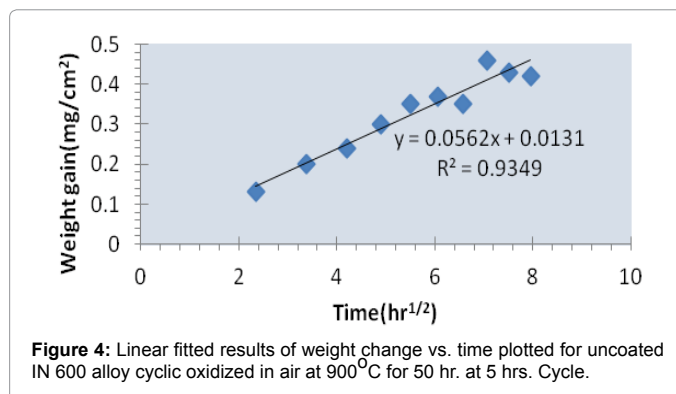

Figure 4: Linear fitted results of weight change vs. time plotted for uncoated IN 600 alloy cyclic oxidized in air at 900°C for 50 hr. at 5 hrs. Cycle.

A large number of voids existing at the scale/alloy interface and in the alloy are observed during the cyclic oxidation of uncoated IN 600 alloy, as shown in Figure 6(a). It is believed that these voids reduce the scale/alloy contact and hence facilitate spalling. These voids may act as concentration sites of thermal stresses induced during heating and cooling leading to crack formation in and spalling of the surface scale. The phases of scale formed on uncoated IN 600 alloy in air after 50 hours at 5 hours cycle at 900°C are Ni, NiO, $(Fe.Cr)_2O_3$ and

$NiFe_2O_4.Cr_2O_3$ appeared at the interface between the alloy matrix and the outer rich in nickel oxide, as shown in Figure 6. When continuous, the NiO layers stop growing, and the oxidation kinetics hardly reflects the growth of the Cr_2O_3 layer. The presence of the spinel $Ni(Fe.Cr)_2O_4$ in the external layer indicates a chemical reaction between NiO and Cr_2O_3 layers as shown in the reaction: $NiO+Cr_2O_3 \rightarrow NiCr_2O_4$ and $NiO+Fe_2O_3 \rightarrow NiFe_2O_4$.

Cyclic oxidation of uncoated IN 600: Both silicon-modified aluminide and Yttria-doped silicon modified aluminide coated IN 600 alloy substrates were subjected to cyclic oxidation. A major goal was to study the kinetic of the oxidation behavior of the coated system at different deposition times as a function of the environment. The specific weight change of the samples with both types of coated systems during the oxidation is plotted as a function of time, as shown in Figure 7.

An obvious scattering is exhibited in the obtained data; this is attributed to the cyclic oxidation behavior. The parabolic oxidation rate constants for four series of experiments are calculated, and the linear lines represent the least squares curve fits to the data in Figure 7. The parabolic oxidation rate constants (kp) for the set of experiments are listed in Table 1.

The kinetic behavior of cyclic oxidation of the coated systems in air, (Si-modified aluminide and Y_2O_3-doped silicon modified aluminide diffusion coating) at 900°C follows the parabolic rate, as depicted in Figure 7.

When coated systems containing Si and Al are exposed to a high-temperature oxidation environment, Al_2O_3 and SiO_2 scales are formed on the surface of the alloy. These scales prevent the rapid oxidation of nickel and iron in the alloy, thereby eliminating the dissolution and inward diffusion of oxygen. Rameshwar et al. [8] confirmed that at higher temperature, the oxidation resistance is frequently lost due
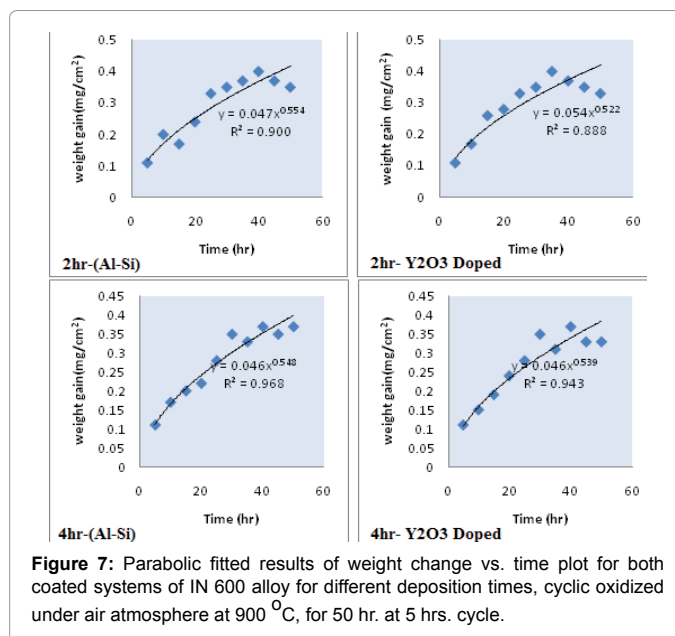

Figure 7: Parabolic fitted results of weight change vs. time plot for both coated systems of IN 600 alloy for different deposition times, cyclic oxidized under air atmosphere at 900 °C, for 50 hr. at 5 hrs. cycle.

Deposition time	n value	Kp (mg2/cm4)/s.
uncoated	0.53	6.58×10-7
2hr, Al-Si	0.55	5.5×10-7
4hr, Al-Si	0.54	5.3×10-7
6hr, Al-Si	0.51	3.38×10-7
8hr, Al-Si	0.49	4.2×10-7
2hr, Al-Si-Y_2O_3	0.52	4.1×10-7
4hr, Al-Si-Y_2O_3	0.53	4.66×10-7
6hr, Al-Si-Y_2O_3	0.47	2.7×10-7
8hr, Al-Si-Y_2O_3	0.46	2.94×10-7

Table 1: n values and oxidation rate constants for cyclic oxidation of coated and uncoated IN 600 alloy in air for 50 hr. at 5 hrs. Cycle at 900°C.
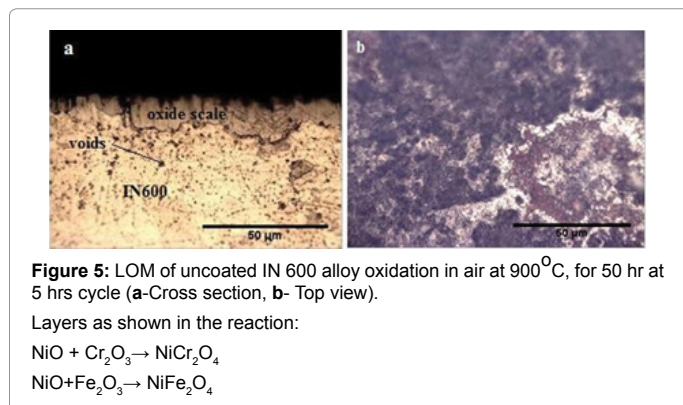
to oxide-scale failure and formation of iron oxides. The addition of Si has been shown to have a favourable effect on maintaining Al_2O_3 rich scale. The presence of Si blocks the rapid diffusion of O_2 through the aluminide layer and thus retards the oxidation of the substrate. Therefore, the effect of Si is clearly due to the concentration of Si at the outer surface of metal and formation of silica layer SiO_2 between the oxide and metal interface. Based on the specific weight change data and the nature of scale formed on the samples, the Y_2O_3 doped silicon modified aluminide diffusion coating showed less weight gain in comparison with silicon-modified aluminide diffusion coating due to the effect of Y, that is noted especially with deposition time 6 and 8 hours Y_2O_3 doped [9]. The XRD analysis determines the intermetallic compounds AlNi and $NiFe_2O_4$, AlNi,α-Al_2O_3 and CrO_3, AlNi and α-Al_2O_3, AlNi and α-Al_2O_3 for samples with deposition time 2, 4, 6 and 8 hours, respectively, for silicon modified aluminide diffusion coatings after cyclic oxidation at 900°C in air for 50 hours at 5 hours for each cycle, manifested in the Figure 8. And, the intermetallic compounds formed for Y_2O_3 doped silicon modified aluminide diffusion coatings for same condition are AlNi and α-Al_2O_3 for 2, 4, 8 hours and AlNi ,$Y_4Al_2O_9$ and α- Al_2O_3 for 6 hours, as shown in the Figure 9. Figures 10 and 11 show the cross-section and top view images of LOM of silicon modified aluminide and Y_2O_3 doped silicon modified aluminide diffusion coating, respectively at deposition times (2,4,6,8) hours, respectively, after cyclic oxidation 50 hours at 5 hours for each cycle in air at 900°C.

Figure 5: LOM of uncoated IN 600 alloy oxidation in air at 900°C, for 50 hr at 5 hrs cycle (**a**-Cross section, **b**- Top view).
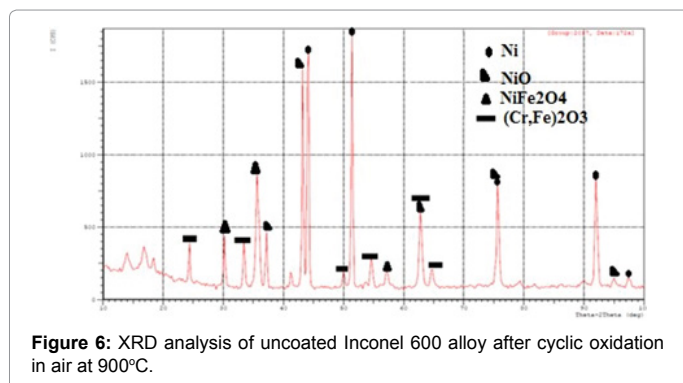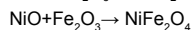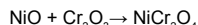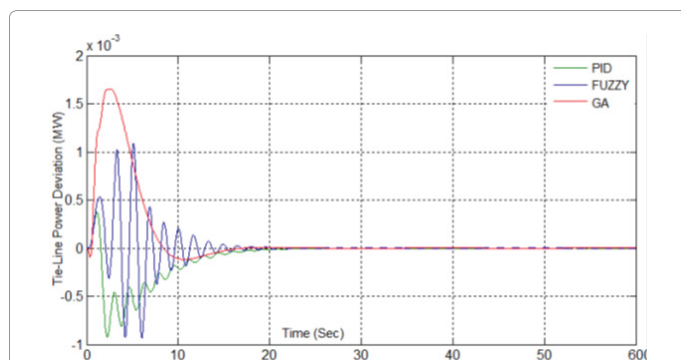
Layers as shown in the reaction:

$NiO + Cr_2O_3 \rightarrow NiCr_2O_4$

$NiO+Fe_2O_3 \rightarrow NiFe_2O_4$

Figure 6: XRD analysis of uncoated Inconel 600 alloy after cyclic oxidation in air at 900°C.

Figure 8: XRD analysis of silicon modified aluminide diffusion coating of Inconel 600 for (2,4,6,8) hrs. at 1120°C after cyclic oxidation in air at 900°C
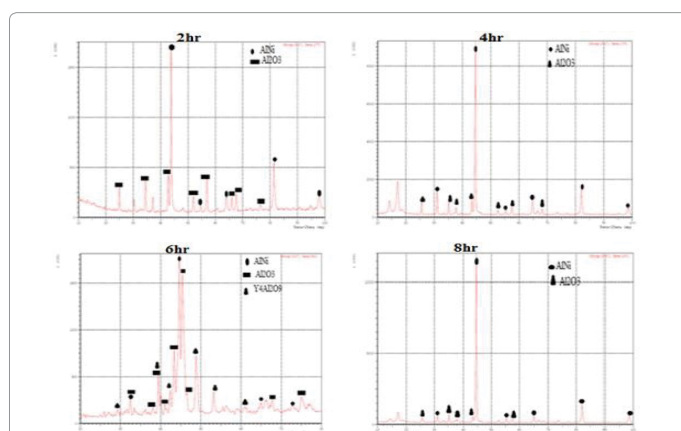

Figure 9: XRD analysis of yttria-doped silicon modified aluminide diffusion coating of Inconel 600 for (2,4,6,8) hrs at 1120°C after cyclic oxidation in air at 900°C.
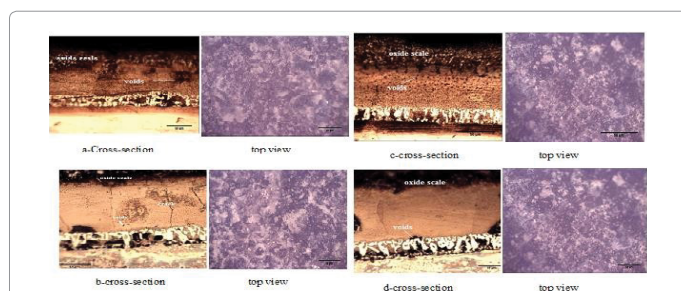

Figure 10: The cross-section and top view images of LOM of silicon modified aluminide diffusion coating at deposition times (2,4,6,8) respectively, after cyclic oxidation 50 hr at 5 hrs for each cycle in air at 900°C.

Figure 11: The cross-section and top view images of LOM of Y2O3-doped silicon modified aluminide diffusion coating at deposition times (2,4,6,8) respectively, after cyclic oxidation 50 hr at 5 hrs for each cycle in air at 900°C.
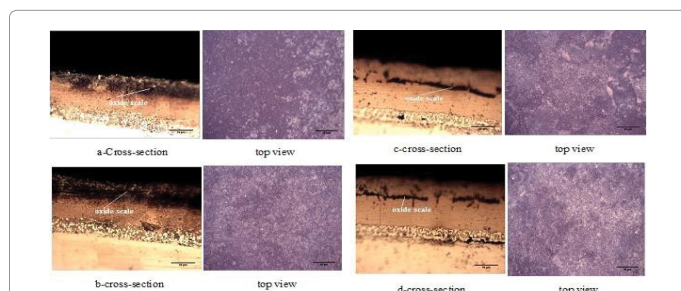
Conclusions

1. The phases formed in the surface layer of as coated specimens for various periods (2,4,6 and 8 hours) of coating time are (Ni_2Al_3, Ni_3Si_2, Ni_2Si, Fe_3Si, $YNi_{10}Si_2$ and Al1.1 Ni0.9).

2. Uncoated IN 600 alloy exhibited parabolic oxidation rate in air at 900°C for 50 hours at 5 hours for each cycle. At this temperature, the oxidation rate is 6.58×10^{-7} (mg^2/cm^4)/s.

3. The major inter-metallic compounds that formed of uncoated IN 600 alloy after cyclic oxidation in air at 900°C for 50 hours at 5 hours for each cycle are Ni, NiO, $(Fe.Cr)_2O_4$ and $NiFe_2O_4$.

4. Both coated systems (Si-modified aluminide and Y_2O_3-doped silicon modified aluminide diffusion coating) have a good cyclic oxidation resistance compared with uncoated IN 600 alloy under the same conditions, and the oxidation kinetics follows the parabolic oxidation rates.

5. The addition of (Y_2O_3) to the alloys reduces the amount of oxide cracks and spalling during the cooling with very little occurrence for the alloys containing 1% Y_2O_3.

6. The best oxidation resistance after 50 hours at 5 hours for each cycle for Y_2O_3 addition is after deposition time 6 and 8 hours. The oxidation rate after deposition time 6 and 8 hours is 2.7×10^{-7} and 2.94×10^{-7} (mg^2/cm^4)/s, respectively.

7. The major inter-metallic compounds that formed in both coated IN 600 alloy (silicon modified aluminide and Y_2O_3 doped silicon modified aluminide diffusion coatings) after cyclic oxidation in air at 900°C for 50 hours at 5 hours for each cycle are $NiFe_2O_4$, CrO_3, α-Al_2O_3, $Y_4Al_2O_9$ and AlNi.

8. It is evident that the presence of the NiAl coating provides a good oxidation resistance.

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