THE EFFECT OF SILICON ON THE OXIDATION OF DUAL PHASE NiAlCrHfY(Si) BOND COAT ALLOYS

by

HANG GAO

Submitted in partial fulfillment of the requirements
For the degree of Master of Science
Thesis Advisor: Dr. Arthur H. Heuer
Department of Materials Science and Engineering
CASE WESTERN RESERVE UNIVERSITY
January 2012
We hereby approve the thesis/dissertation of

HANG GAO

candidate for the _____ Master of Science _____ degree. *

(signed) ___________ Arthur H. Heuer
(Chair of the committee)

___________ Gary M. Michal

___________ James D. McGuffin-Cawley

(date) ___________ Sep. 28 2011

*We also certify that written approval has been obtained for any
proprietary material contained therein.
DEDICATION

The author wishes to express her gratitude to her parents, her father Guoying Gao and her mother Xie Zhou, for their endless love and understanding.
# TABLE OF CONTENTS

CHAPTER 1 INTRODUCTION ........................................................................... 1

WORKS CITED................................................................................................. 5

CHAPTER 2 BACKGROUND............................................................................... 6

2.1 Design of the bond-coat and TGO in the TBC system.............................. 7

2.2 Oxidation mechanism for RE-induced alloys........................................ 13

2.2.1 Transport of Oxygen and Aluminum during oxidation.................... 13

2.2.2 Effect of reactive elements on the Al₂O₃ scale growth....................... 18

2.3 Previous investigations of the Si effect on the oxide growth.................. 21

WORKS CITED................................................................................................. 24

CHAPTER 3 EXPERIMENTS........................................................................... 27

3.1 Standardized Experimental Procedures .................................................. 28

3.1.1 Sample preparation of Ni-20Al-5Cr-0.05Hf-0.05Y-(1Si)......................... 29

3.1.2 Identification of crystal orientation by EBSD work.......................... 30

3.1.3 Oxidation in hot stage.......................................................................... 31
3.2 Analytical instruments........................................................................................................34

WORKS CITED..........................................................................................................................39

CHAPTER 4 RESULTS..............................................................................................................40

4.1. Orientation effect of the substrate alloys on the oxide scale growth.........................41

4.2 Oxidation of NiAlCrHfY(Si) at 950°C for 1 minute......................................................48

4.3 Oxidation of NiAlCrHfY(Si) at 1150°C for 1 minute......................................................48

4.4 Oxidation of NiAlCrHfY(Si) at 1150°C for 30 minutes.................................................54

WORKS CITED..........................................................................................................................62

CHAPTER 5 DISCUSSION.......................................................................................................63

5.1 Evolution in the chemistry and microstructure of the oxide scale............................64

5.2 Effect of Si on the evolution of layered oxide ..............................................................69

WORKS CITED..........................................................................................................................72

CONCLUSION.........................................................................................................................74

FUTURE WORKS....................................................................................................................76
LIST OF TABLES

Table 2.1 oxidation results for several other alloy compositions, which were chosen to confirm the oxide map in Figure 2.2.................................................................12

Table 3.1 Alloy compositions used in experiments..................................................30

Table 3.2 Energy values of X-ray for Hf, Si and Y....................................................34

Table 4.1 Atomic percentages of O, Al, Ni, Cr at Areas 1, 2, 3, 4 and 5 from Fig. 4.9.................................................................................................................................56

Table 4.2 Atomic percentages of contained elements at Areas 1, 2, 3, 4, 5, 6 from Fig. 4.10...............................................................................................................................59

Table I-1 Atomic percentages of the elements contained at Areas 1, 2, 3, 4 and 5 from Fig.I-1........................................................................................................................78
LIST OF FIGURES

Figure 1.1 Cross-sectional scanning electron micrograph (SEM) image of the thermal barrier coating used on a turbine blade, which overlapped on a schematic diagram showing the temperature gradient through the TBC system. ........................................4

Figure 2.1 Schematic diagram shows the formation of new oxide in the scale grain-boundaries. The volume expansion because of the lateral growth of new oxide leads to compressive stresses.................................................................11

Figure 2.2 Oxide map of Ni-Al-Cr ternary system at 1000°C. .................................49

Figure 2.3 Effective (boundary) diffusivity deduced from oxidation rates compared to the boundary diffusivity of oxygen estimated by Gordon et al.......................17

Figure 2.4 The effect of oxygen partial pressures ($P_{O_2}$) on the $D_{gb}^\delta$ and $D_{gb}^{\text{Al}}$ in the Al$_2$O$_3$ scale with and without reactive element doped. The diagram shows that at a high $P_{O_2}$, Al diffusion dominates; at a low high $P_{O_2}$, O diffusion dominates. Addition of Lu$_2$O$_3$ only influence the $D_{gb}^\delta$.................................................................20

Figure 2.5 Cyclic weight gains over one thousand 1-hr cycles at 1150°C in air, which shows the Si effect on oxidation behavior of co-doped $\gamma$-Ni+$\gamma'$-Ni$_3$Al alloys..................23

Figure 2.6 Cross sectional SEM images of oxide scale microstructures: (a) $\gamma$-Ni+$\gamma'$-Ni$_3$Al-0.05Hf-0.05Y (b) $\gamma$-Ni+$\gamma'$-Ni$_3$Al-0.1Hf-0.05Y (c) $\gamma$-Ni+$\gamma'$-Ni$_3$Al-0.1Hf-0.05Y-1Si (d) $\gamma$-Ni+$\gamma'$-Ni$_3$Al-0.05Hf-0.05Y-1Si after cyclic oxidation in Fig. 2.5.............23

Figure 3.1 A series of standardized experimental procedures .................................29
Figure 3.2 Oxidation instruments: (a) Hot stage, (b) schematic cross section of hot stage……………………………………………………………………………………………………32

Figure 3.3 Three conditions for oxidation used in the experiments……………………32

Figure 3.4 Schematic shapes of electron interaction volumes…………………………36

Figure 4.1. NiAlCrHfY: (a) stereographic triangle, which is the color key for image (b); (b) EBSD inverse pole figure (IPF) map of grains normal to the plane, two individual grains are indicated as G1 and G2; (c) SEM plan view of the oxide after oxidation in 1150°C for 1min in air; fewer submicron nodules were found on G1 (Z close to <001>) relative to G2…………………………………………………………………………………………………42

Figure 4.2 NiAlCrHfYSi: (a) stereographic triangle as the color key for (b); (b) EBSD inverse pole figure (IPF) map of grains normal to the plane, a rectangle region (black frame) contains three individual grains indicated as G1 (<001>-orientated), G2 (<101>-orientated) and G3 (<111>-orientated); (c) SE plan view image of the oxide after oxidation in 1150°C for 1 min, less Ni-rich oxide was found on G3; SE image was taken under an accelerating voltage of 5kV. (d) SE image was taken at the same region of that shown in (c), but under an accelerating voltage of 15kV……………………………………45

Figure 4.3 Cross-sectional SEM image of alloys with the grain orientation close to <001> after oxidation at 1150°C for 1 min: (a) NiAlCrHfY (b) NiAlCrHfYSi………………………46

Figure 4.4 Cross-sectional STEM-EDX elemental maps of NiAlCrHfY oxidized at 950°C for 1 minute, showing the oxide scale consists of an outer NiO layer, an inner Al₂O₃ scale and Cr-containing oxide within the scale……………………………………………………………49
Figure 4.5. Cross-sectional STEM-EDX elemental maps of NiAlCrHfYSi oxidized at 950°C for 1 minute, showing the oxide scale consists of an single Al$_2$O$_3$ scale and Cr-containing particles in the inner part of the Al$_2$O$_3$ scale............................................50

Figure 4.6 Cross-sectional STEM-EDX elemental maps of NiAlCrHfY oxidized at 1150°C for 1 minute, showing the oxide scale consists of the top NiO, the middle Ni(Cr,Al)$_2$O$_4$/Cr$_2$O$_3$ and the inner most Al$_2$O$_3$.................................................................51

Figure 4.7 Cross-sectional STEM image and its EDS elemental maps of NiAlCrHfYSi oxidized at 1150°C for 1 min, revealing the oxide scale mainly consists of a single Al$_2$O$_3$ scale, which includes higher Ni content in the outer part of the Al$_2$O$_3$ scale and higher Cr content at the inner part of the Al$_2$O$_3$ scale.................................................................52

Figure 4.8 Cross-sectional STEM-EDX elemental maps of NiAlCrHfY oxidized at 1150°C for 30 minutes, revealing that the oxide scale consists of an outer NiO/spinel, an inner Al$_2$O$_3$ scale with some Cr$_2$O$_3$/spinel inside.........................................................55

Figure 4.9 Cross-sectional STEM image of NiAlCrHfY oxidized at 1150°C for 30 minutes; elemental quantitative analysis on Area 1, 2, 3, 4, 5 has done by XEDS and are marked by blue rectangles.................................................................56

Figure 4.10. STEM image of cross-sectional oxide scale on NiAlCrHfYSi after heating at 1150°C for 30 minutes in air. (A) Pt deposition, (B) Pd deposition, (C) the oxide scale (mostly Al$_2$O$_3$), (D) substrate alloy. Elemental quantitative analysis on Area 1, 2, 3, 4, 5, 6 has been performed by XEDS, which are marked by red circles.......................57

Figure 4.11 Cross-sectional STEM-EDX elemental maps of NiAlCrHfYSi oxidized at 1150°C for 30 minutes, revealing that the oxide scale mainly consists of a single Al$_2$O$_3$
scale and some nano-size Ni-rich particles are embedded at the inner part of the Al₂O₃ scale..........................................................................................................................58

Figure 5.1 The phase diagram of Ni-Al-O at 1000°C proposed by Elrefaie..................65

Figure 5.2 Schematic diagram of the evolution of layered oxides formed on γ/γ’-NiAlCrHfY(Si) alloys......................................................................................................................66

Figure 5.3 Elemental maps by TOF-SIMSI, alloys were heated at 1100°C for 50min in air: a) Hf intensity from the oxide scale of NiAlCrHfY; b) Y intensity from the oxide scale of NiAlCrHfY; c) Hf intensity from the oxide scale of NiAlCrHfYSi; d) Y intensity from the oxide scale of NiAlCrHfYSi.................................................................69

Figure I-1. NiAlCrHfY oxidized at 1150°C for 30 mins in air: (a) Cross-sectional STEM image on the oxide scale; Small particles (Area 1,2) with high contrast are observed in the oxide scale; (b) the XED spectrums of Area 1 and 3 were indicated by yellow area and red line, respectively; (c) the XED spectrum for Area 2.................................77

Figure II-1. Backscattered electron (BSE) image of NiAlCrHfYSi before oxidation....81

Figure II-2. 0° tilted SEM images with lower magnification showed the surface morphologies of (a) NiAlCrHfY, (b) NiAlCrHfYSi after oxidation at 1150°C for 1min.................................................................81

Figure II-3. 52° tilted SEM images showed the surface morphologies after oxidation at 1150°C for 1min: (a) NiAlCrHfY, (b) NiAlCrHfYSi.................................82

Figure II-4. STEM-EDX elemental maps of the micron-size nodules formed on NiAlCrHfYSi after oxidation at 1150°C for 1min.................................................................82
Figure III-1. (a) Cross-sectional STEM image of the oxide scale and the grain boundary of NiAlCrHfY after heating at 1150°C for 1min in air. (b) STEM image of the yellow frame with higher magnification than (a). EDX line-scan across the grain boundary of the bulk material, the dark red line and green line indicate the content variations of Y and Hf, respectively. (c) EDX line-scan along the yellow arrow in (b)……………………………85

Figure III-2. (a) STEM image of cross-sectional NiAlCrHfYSi on the grain boundary after heating at 1150°C for 1min. (b) EDX line-scan along the yellow arrow in (a)……86
ACKNOWLEDGEMENTS

This research project would not have been possible without the support of many people.

The author wishes to express her gratitude to:

Professor Arthur H. Heuer
Professor Gary M. Michal
Professor James D. McGuffin-Cawley
Professor Brian Gleeson
Dr. David Hovis
Dr. Reza Sharghi-Moshtaghin
Dr. Amir Avishai
Nanthawan Avishai
Dr. Wayne Jennings
Dr. Jason Wang
Dandan Wu
Danqi Wang
Hao Qu
Claire Chen
The Effect of Silicon on the Oxidation of Dual Phase NiAlCrHfY(Si) Bond Coat Alloys

Abstract

by

HANG GAO

Research has been conducted on the dual phase $\gamma/\gamma'$-NiAlCrHfY(Si) bond coat alloys to determine the effect of 1 at.% of silicon on the evolution of the oxide scale at an early stage of oxidation. The microstructures of oxide scales formed on selected grains of NiAlCrHfY(Si) alloys are compared in this work. Instead of forming an exclusively $\alpha$-Al$_2$O$_3$ scale, NiAlCrHfY alloys form NiO/spinel as the top layer of the scale and Al$_2$O$_3$ as the bottom layer of the scale, with some voids within the oxide scale and at the Al$_2$O$_3$/alloy interface. NiAlCrHfYSi alloys form a mostly Al$_2$O$_3$ scale with a small amount of Ni content in the outer part and Ni-rich particles at the inner part. The addition of silicon promotes formation of a scale with less included NiO/spinel and fewer voids; this beneficial effect arises from decreasing the outward diffusion of Ni from the alloy. However, the addition of Si does not prevent void formation at the Al$_2$O$_3$/alloy interface.

Some other factors such as grain orientation of the alloy could also influence the formation of the oxide scale. In order to exclude the grain orientation effect, the grain orientation has been determined on the NiAlCrHfY(Si) alloys by EBSD before oxidation. The grains of NiAlCrHfY(Si) with an orientation close to $<001>$ were chosen to be studied in this work. Then NiAlCrHfY(Si) alloys were oxidized under a series of
oxidation conditions: 950°C with a hold time of 1 minute; 1150°C with a hold time of 1 minute; 1150°C with a hold time of 30 minutes. STEM-EDS mapping and quantitative analysis were used to study the microstructural evolution and elemental composition of the scales on the NiAlCrHfY(Si) alloys.
CHAPTER 1

INTRODUCTION
Over the past several decades, the development of gas turbine technology has led to the design of more powerful and more efficient engines. One of the significant improvements is the increase of maximum gas temperature in the turbine engine. Currently, turbine engines, which are used in military aircraft, can be operated with gas temperatures up to 1600°C. Turbine engines for commercial use have an operating gas temperature of up to 1500°C [1]. These increases in temperature increase the efficiency of engines; on the other hand, the nature of the engine materials restricts the operating temperature from reaching a higher level.

Ni base superalloys, which are the dominant material used in turbine engines, have a melting point around 1300°C, below the operating temperature of gas turbine engines. The thermal barrier coating system (TBC system) has thus been designed to limit thermal exposure, which provides a temperature gradient and also protects the surface material of the alloy from oxidation by the hot gas, whether in the turbine or the combustor. [2] A TBC system provides the optimum operating temperature limits and maximizes the lifetime of engine components, as well as energy efficiency. [3] An image of a thermal barrier coated turbine blade is shown on the left in Figure 1.1. On the right, the scanning electron micrograph (SEM) cross-sectional image shows the multilayer structure of the thermal barrier coating. This SEM image is superimposed onto a schematic line chart, which shows the temperature gradient through the TBC system. The temperature of the hot gas decreases from the top surface down to the inner substrate due to the TBC. The TBC system has four layers: the top two layers are ceramic; the other two layers are metallic. From top to inner material, these layers are (i) the ceramic top-coat, (ii) the thermally-grown oxide (TGO), (iii) the bond-coat (BC) and (iv) the superalloy substrate.
Typically, the ceramic top-coat layer consists of $\text{Y}_2\text{O}_3$-stabilized $\text{ZrO}_2$ (YSZ) which provides the thermal insulation from the hot gas. The bond-coat is an oxidation-resistant metallic layer, which is typically made of a MAICrY alloy (M= Ni, Fe and/or Co) with a thickness of 75 to 150 μm. [4] When the temperature of gas-turbine engines increases to 700°C, or above during operation, another ceramic layer— the thermally grown oxide (TGO) with a thickness of 1 to 10μm forms between the bond-coat layer and the top-coat layer, because of the oxidation of the bond-coat. [5].

An ideal TGO should be an exclusively $\alpha-\text{Al}_2\text{O}_3$ layer, which grows uniformly, slowly, and without defect. Such a TGO is an excellent diffusion barrier, which has low oxygen diffusivity and retards further oxidation of the bond-coat. [6] The further oxidation of the bond coat is not only controlled by the inward diffusion of oxygen through the TGO, but in some cases, it is also controlled by the Al outward diffusion, and results in the formation of new TGO at the interface between the TGO and the bond coat or at the grain boundaries within the TGO [5,6,8].

Currently, many MCrAlY coatings with different compositions are commercially available. Different dopants, e.g. Y, which are known as reactive elements (RE), are added to improve the high temperature resistance of the coatings. [7] For instance, Ta is a dopant used to improve hot corrosion resistance [9, 10]. The addition of Hf or some other RE dopants was already reported to improve the oxidation behavior [11]. As a result, the effects of these RE dopants provide much economic benefit. In this study, we mainly focus on the effects of reactive elements, especially Si, on the scale growth of TGO.
Figure 1.1 Cross-sectional scanning electron micrograph (SEM) image of the thermal barrier coating used on a turbine blade. The schematic diagram shows the temperature gradient through the TBC system.
WORKS CITED


CHAPTER 2

BACKGROUND
The bond-coat is designed to form a protective $\alpha$-Al$_2$O$_3$ scale during oxidation in order to improve the oxidation resistance of the TBC system. It has been reported that the process of the oxide film growth (mostly Al$_2$O$_3$) is generally controlled by the transport of oxygen and aluminum along the grain boundaries of the Al$_2$O$_3$ scale. The influence of impurities (such as Hf, Y, Si) on oxide scale growth, which is also called the “reactive element effect,” is of considerable importance because these reactive elements improve oxidation resistance. It has been hypothesized that one of the significant roles of these reactive elements is to influence the electronic structure of near-band-edge grain boundary states in the Al$_2$O$_3$ scale. [1]

2.1 Design of the bond-coat and TGO in the TBC system

In order to improve the energy efficiency and the durability of the TBC system, the requirements for the designation of the bond-coat (BC) and TGO contain the following aspects: (1) the bond-coat forms $\alpha$-Al$_2$O$_3$ as the main content of the TGO in high temperature oxidation; (2) the TGO has uniform morphology, controlled defects and the lowest thickness; (3) the TGO should be adherent with the BC. [2] $\alpha$-Al$_2$O$_3$ is the ideal TGO because of its relatively high negative free energy of formation and its low diffusion coefficients for anions and cations. [3]

However, there are still some problems in the design of the bond-coat and TGO. The MCrAlX type alloys, where “M” represents the base metal Fe, Ni and/or Co, “X” represents the reactive elements Hf, Y, Zr and/or other alloying elements, contain the oxide of the base metal and this oxide remains in the final scale after oxidation. [4] However, the oxides of the base metals (FeO, NiO and CoO) cannot fulfill the
requirements of the TGO because these oxides have low free energy of formation, high diffusion coefficients for cations and low melting temperatures. The extent of base metal oxide formation depends highly on the oxidation temperature, the environmental oxygen partial pressure and the alloy composition. [5]

One major disadvantage of the Al₂O₃ scale is that it easily spalls from the alloy, particularly during cyclic oxidation. One explanation for the scale spallation is the difference between the thermal expansion coefficients of the Al₂O₃ scale and the alloy. The thermal expansion coefficients of alloys Fe27Cr4Al, NiAl and FeAl are 14×10⁻⁶/°C, 15×10⁻⁶/°C, and 16.5×10⁻⁶/°C, respectively. But, the thermal expansion coefficient of Al₂O₃ is 9×10⁻⁶/°C. [6] Because of the thermal expansion mismatch between Al₂O₃ and the bond coat, they must have strain compliance to withstand the mismatch during thermal cycling. Without strain compliance, the large stress caused by elastic mismatch would finally lead to the failure of the TGO. Researchers have paid much attention to this phenomenon, which is also called “TGO spallation”. However, the interfacial adhesion of the Al₂O₃ scale to the alloy is not strong enough to overcome the stresses and lead to “TGO spallation”. [7] In addition, Stott [6] and Hou [8] have reported that a significant contribution from a small amount of outward diffusion of Al is the scale lateral growth, causing residual compression and finally leading to the wrinkling or the detachment of the scale from the substrate (see Fig.2.1).

Therefore, the improved TGO and BC will play an important role in meeting the requirements of the TBC system for improving energy efficiency and durability. We have seen that the keys to accomplish the improvement are promoting the formation of α-
Al₂O₃ as the TGO but not some other base metal oxide, and then maintaining a strong bond between the α-Al₂O₃ scale and alloy. It is also desirable to reduce the diffusion rate of both Al and O. Choosing the bond-coat composition can be helpful. [9] For the MCrAlX type alloys, the ratio of base metal M and element Al, Cr can be varied in order to form an α-Al₂O₃ scale. For example, Kofstad reported that the about 20 at. % of Cr addition reduces the amount of Al to no more than 10 at. % that is necessary to establish an Al₂O₃ scale. [10] The species and the amount of reactive element X can be varied to affect the outward diffusion of Al and inward diffusion of O, and then slow down the scale thickening and improve the scale adhesion. The effect of reactive elements on the diffusion process will be discussed further in the next section.

Over recent decades, researchers have constructed some basic oxidation mechanisms related to the complex reactions between alloys and oxidizing gases at high temperatures. It is very important to select suitable ternary compositions in order to form protective oxide scales (α-Al₂O₃) during oxidation. Kosak and Rapp [11] plotted an “oxide map” by superimposing oxidation data onto a Ni-Al-Cr ternary phase diagram at 1000°C which indicates the suitable compositions of alloys as high temperature coatings (Fig.2.2). The oxides have been divided into three types: 1. external NiO and internal oxide (Cr₂O₃, Al₂O₃ and/or spinel lie between external NiO and alloy); 2. external Cr₂O₃ and internal oxide; 3. external Al₂O₃. At least 10 at. % Al is required for the formation of external Al₂O₃ according to the oxide map. The experimental data in Table 2.1 confirm the oxide map in Fig. 2.2. One of the limitations of the oxide map is that it is empirically determined by experimental data, which may be affected by the experimental conditions. The position of the separating lines for different region on the oxide map may then vary.
slightly. Moreover, there are still some areas in the oxide map that have unpredictable performance after oxidation. For example, in Table 2.1 Alloy C has 75 at. % of Ni, 20 at. % of Al and 5 at. % of Cr, which forms $\text{Al}_2\text{O}_3$ and NiO after oxidation at 1000°C according to the experimental data. However, according to the oxide map, only external $\text{Al}_2\text{O}_3$ forms on Alloy C. The oxidation data mentioned above were determined by X-ray diffraction and metallographic techniques, without any microstructure data. [3]

Moreover, Wright [12] reported that the single-phase $\beta$-(Ni,Pt)Al could represent a class of the bond coat in the TBC system. The depletion of Al occurs in the single-phase $\beta$-(Ni,Pt)Al, which results from the formation of the $\text{Al}_2\text{O}_3$ scale and the interdiffusion with the superalloy substrate, leads to the transformations of the $\beta$ phase to the phases that contain more Ni, e.g. $\gamma'$-Ni$_3$Al and martensite. [13, 14] The volume changes that occur during the phase transformations could result in rumpling at the surface of the $\beta$ phase alloys and then affect their ability to maintain the adherence of an $\text{Al}_2\text{O}_3$ scale. [15] Gleeson et al. [16,17,18] reported that the $\gamma/\gamma'$-based Ni-20Al-22Pt-7Co-7Cr-0.7Hf (at.%) formed an adherent $\text{Al}_2\text{O}_3$ scale with reduced rumpling after cyclic oxidation. Rae [19] demonstrated that the $\gamma/\gamma'$ structure, which has a significant effect on the creep properties, is the basis of the excellent mechanical properties of the superalloys. Therefore, two $\gamma/\gamma'$-based alloys were deemed of interest in our study based on the previous investigations.
Figure 2.1 Schematic diagram shows the formation of new oxide in the scale grain-boundaries. The volume expansion because of the lateral growth of new oxide leads to compressive stresses.
Figure 2.2 Oxide map of Ni-Al-Cr ternary system at 1000°C.

Table 2.1 oxidation results for several other alloy compositions, which were chosen to confirm the oxide map in Figure 2.2.
2.2 Oxidation mechanism for RE-induced alloys

2.2.1 Transport of Oxygen and Aluminum during oxidation

When an alloy is exposed to a high temperature oxygen-containing atmosphere, the oxidation starts with the adsorption of oxygen to the surface to the alloy. The alloy then reacts with the adsorbed oxygen atom and forms nuclei of oxide. Oxide corrosion films (Al₂O₃) are formed on the alloy surface, which can protect the alloy from rapid oxidation. The thickening of the Al₂O₃ scale is controlled by both inward diffusion of oxygen and outward diffusion of Al³⁺ ions. This mechanism provides a coupling model of outward and inward transport during oxidation. However, the mechanism for scale growth is complicated and many things related to counter diffusion of Al and O are still not very clear. Moreover, it becomes even more complicated considering that there are several transitional Al₂O₃ phases formed before the formation of the most stable α-Al₂O₃. For example, Manen et al. [19] and Graham et al. [20] reported that the growth of metastable γ-Al₂O₃ and θ-Al₂O₃ is probably mainly controlled by the outward diffusion of Al³⁺ ions. Therefore, we will mainly discuss the diffusion process in the α-Al₂O₃ scale in this section.

Once a continuous oxide layer forms, the kinetics of oxide formation mostly depend on the properties of the oxide films. The thickening rate of the oxide film decreases as the films thicken. Oxidation models can be classified by three characteristic rate equations: linear, logarithmic and parabolic. [21] The parabolic rate equation is frequently used when encountering multi-layer oxide films at high temperatures. The
parabolic rate equation would be described as the oxide growth rates, which is inversely related to the thickness of the oxide film. The growth of an Al$_2$O$_3$ scale follows parabolic kinetics. Stott [6] and Hou [8] have reported the short-circuit paths, probably the grain boundaries of the Al$_2$O$_3$ scale, which have always been considered the main transport pathways due to the small grain sizes of Al$_2$O$_3$ (about 0.5~2μm). Hence, the parabolic rate constant for the growth of Al$_2$O$_3$ scale could be described by the following equation:

\[ k_p = \int_{P_{O_2}} \left[ 1.5\left(D_{L\,Al} + \frac{\delta D_{b\,Al}^2}{d}\right) + \left(D_{L\,O} + \frac{\delta D_{b\,O}^2}{d}\right) \right] \, d \ln P_{O_2} \]  

(1)

where \( k_p \) is the parabolic rate constant. \( \delta \) is thickness of the diffusion layer, which depends on the diffusion coefficient \( D \). \( D_{L\,Al} \) and \( D_{L\,O} \) are the lattice diffusivities of Al and O, respectively. \( D_{b\,Al} \) and \( D_{b\,O} \) are the boundary diffusivities of Al and O, respectively. \( d \) is the Al$_2$O$_3$ grain size. \( P_{O_2} \) is the oxygen potential difference through the Al$_2$O$_3$ scale. A combination of the boundary diffusivities of O and Al is described as an effective diffusivity, \( D_{eff} \), in the following equation:

\[ D_{eff} = k_p d \left( \ln P_{O_2} \right) \]  

(2)

Equations (1), (2) are based on several assumptions: first, \( D_{eff} \) are not functions of \( P_{O_2} \); second, the contribution from lattice diffusion to the oxide growth is insignificant. Hou [8] calculated the range of \( D_{eff} \) using Equ.(2) and the range of \( k_p \) calculated by Equ.(1). Gordon et al. [22, 23] have estimated the value of \( D_{b\,O}^2 \delta \) at 1450°C, which is in the range of \( 10^{-14} \) to \( >10^{-13} \) cm$^2$/s. The estimated value of \( D_{b\,O}^2 \delta \) agrees well with
the upper bound of $D_{\text{eff}}$ deduced from equation (1) and (2) (see Fig. 2.3). It has been well known that oxidation is controlled by the species (O and/or Al) that have the faster diffusing rate, along the fastest diffusion path. Therefore, a critical question related to $D_{\text{eff}}$ is the relative contribution of Al and O transport to the growth of oxide scales during oxidation.

However, it is not easy to summarize the relative contribution of Al and O transport. The oxygen permeability experiments reported by Matsudaira et al. [24] and reviewed by Heuer et al. [1] indicated that the grain boundary diffusion coefficients of oxygen, $D_{\text{g0}}$, determined at $P_{O_2}=10^{-7}$ Pa while the grain boundary diffusion coefficients of aluminum, $D_{\text{gA}}$, determined at $P_{O_2}=10^5$ Pa. Kitaoka et al. [25] reported that $D_{\text{g0}} > D_{\text{gA}}$, at a range of oxidation temperature between 1000-1200°C, ignoring that these data for Al and O diffusion are collected at different oxygen partial pressures ($P_{O_2}$).

Most recently, a new theory reported by Heuer et al. [1] indicated that the “new” $\text{Al}_2\text{O}_3$ formation mechanism could be affected by the electronic structure of $\text{Al}_2\text{O}_3$ during oxidation. In a high oxygen partial pressure ($P_{O_2}$), $\text{O}_2$ molecules become lattice oxygen and Al vacancies migrate to the low $P_{O_2}$ surface. In contrast, Al ions diffuse from the low $P_{O_2}$ surface to the high $P_{O_2}$ surface and react with oxygen to form “new” $\text{Al}_2\text{O}_3$. The electronic structure of the $\text{Al}_2\text{O}_3$ scale is described as p-type. In a low $P_{O_2}$, $\text{O}_2$ molecules are reformed by Al vacancies and lattice oxygen. The electronic structure of this type of $\text{Al}_2\text{O}_3$ scale is described as n-type. The reactions occur in the p-type (equ. (3)) and n-type (equ. (4)) structures are showed as follows:
\[
\frac{1}{2}O_2 \rightarrow O_0^- + \frac{2}{3}V_{\text{Al}}'' + 2h^*
\]  

(3)

\[
O_0^- \rightarrow \frac{1}{2}O_2 + V_{\text{O}}^* + 2e'
\]  

(4)

where \(O_0^-\) is lattice oxygen, \(V_{\text{Al}}''\) and \(h^*\) are Al vacancies and holes respectively. \(V_{\text{O}}^*\) is oxygen vacancies. A transition from p type to n type occurs within the scale and the formation of a measurable level of \(\text{Al}_2\text{O}_3\) scale is possible. [1]
Figure 2.3 Effective (boundary) diffusivity deduced from oxidation rates compared to the boundary diffusivity of oxygen estimated by Gordon et al. [22, 23].
2.2.2 Effect of reactive elements on the Al$_2$O$_3$ scale growth

It has been known for many years that reactive elements (Y, Zr, Hf, etc.) have significant effects in improving the high temperature resistance of oxide scales in the following several aspects: (1) the addition of reactive element can retard the kinetics of the transformation from metastable $\theta$- Al$_2$O$_3$ to stable $\alpha$-Al$_2$O$_3$ [1]; (2) the configuration of the scale can be changed by adding reactive element; scale convolution or wrinkling is rarely found on alloys containing reactive elements [6]; (3) the addition of reactive element generally lowers the parabolic oxidation rate of new oxide within the scale [1]. Several types of reactive elements added into different types of alloys have been found to segregate at the grain boundaries. Hou [13] has reported that about a factor of 2 of the oxidation rate was reduced by the addition of the RE (Hf, Y, Zr, La) in Fe- and Ni-based alloys. The addition of Zr in a PtAl alloy reduced the oxidation rate by a factor of 4. The addition of Y and La [13, 14] reduces $D^0$, but it does not have a significant effect on $D^0$.

Matsudaira et al. [24] have reported the oxygen permeability experiments on Al$_2$O$_3$ with the addition of Hf and 0.2 m/o Lu$_2$O$_3$, which was reviewed by Heuer [1]. The $D^0_{gb}$ value in the Al$_2$O$_3$ doped with 0.2 mol.% Lu$_2$O$_3$ decreased three times, relative to the $D^0_{gb}$ value of the undoped sample. The undoped sample, and the sample doped with 0.2 mol.% Lu$_2$O$_3$ have almost the same value of $D^0_{gb}$ in Al$_2$O$_3$. The addition of Hf decreases the value of $D^0_{gb}$, but has no significant effect on the value of $D^0_{gb}$ (Figure 2.4). In addition, Matsudaira et al. [24] have also reported that the $D^0_{gb}$ value in the Al$_2$O$_3$ doped with 0.05 mol.% Lu$_2$O$_3$ is almost the same as that in the undoped sample, which was not plotted in Figure 2.3. These indicated that the effect of reactive elements on the diffusion
of O and Al in Al₂O₃ is very complicated, and depends on the species and the amount of the reactive elements. The “electronic structure” theory offered by Heuer et al. [1] indicated that the reactive element improves the oxidation resistance of Al₂O₃ scale by affecting the electronic structure of Al₂O₃, rather than blocking the short circuit pathways (grain boundaries within the Al₂O₃ scale). In the “electronic structure” theory, the dopant helps to decrease the injection of Al vacancies and ionization of Al into the scale by modifying the donor and acceptor states at Al₂O₃ grain boundaries, and then finally inhibits the formation of “new” Al₂O₃.
Figure 2.4 The effect of oxygen partial pressures ($P_{O_2}$) on the $D_{gb}^o\delta$ and $D_{gb}^{Al}\delta$ in the $Al_2O_3$ scale with and without reactive element doped. The diagram shows that at a high $P_{O_2}$, Al diffusion dominates; at a low high $P_{O_2}$, O diffusion dominates. Addition of $Lu_2O_3$ only influence the $D_{gb}^o\delta$. 
2.3 Previous investigations of the effect of Si on oxide growth

There is a limitation on oxidation resistance of oxide scales formed on pure metals or alloys in a hot oxidizing environment. The addition of reactive elements into the alloys may further improve the oxidation resistant by improving the scale adhesion and limiting the rate of scale growth. [29] Professor Brian Gleeson (University of Pittsburgh) has done much work on high-temperature degradation of metallic alloys and coatings. The curves of weight grains over cyclic oxidation were plotted by Dr. Gleeson’s research group, which are shown in Fig. 2.5. According to their study, \( \gamma\)-Ni+\( \gamma'\)-Ni3Al alloys doped with different reactive elements were compared by weight change curves. The red line which indicated \( \gamma\)-Ni+\( \gamma'\)-Ni3Al alloy doped with 0.05 at.% Hf, 0.05 at.%Y and 1 at.% Si exhibits the minimum weight change. After about 860 thermal cycles, scale spallation occurs on both \( \gamma\)-Ni+\( \gamma'\)-Ni3Al-0.05Hf-0.0Y (shown by blue curve) and \( \gamma\)-Ni+\( \gamma'\)-Ni3Al-0.1Hf-0.0Y (shown by pink curve) alloys. Figure 2.6 shows the scale microstructures of four types of alloys, NiAl-0.05Hf-0.05Y-1Si formed the thinnest oxide scale without any internal oxides. Therefore, according to the study of Dr. Gleeson, the addition of Si slows down the oxidation rates of co-doped alloys. Wu, Gesmundo and Niu [30] reported the beneficial effect of Si on the oxidation of Ni-xSi-6Al at 900°C for 24h. According to their study, Si helps to promote the growth of a protective alumina-rich layer at the bottom of the scale, and then prevents the formation of internal oxidation. The oxidation resistance of the coatings is increasing in the following order: \( \text{Cr}_2\text{O}_3 < \text{Al}_2\text{O}_3 < \text{SiO}_2\). [31] Han et al. reported that SiO\(_2\) is usually amorphous in the oxide scale and does not have the potential for the short circuit diffusion, which contributes to the scale growth. [32] Moreover, the oxidation behavior of Ni-Si-4at.%Al alloys were
investigated at 800°C under 1atm and 5-9×10⁻⁶ atm O² by Yi et al.[33] They reported the addition of Si increased the oxidation rate during the early stages of oxidation, but decreased the rate at longer times by forming a top NiO layer, the double oxides (NiAl₂O₄ and Ni₂SiO₄) and a region of internal oxides.

The work done by previous researchers has already proved the positive effect of Si on the oxidation behavior of Ni-Al-Cr ternary alloy. In this article, at an early stage of oxidation, the effect of Si on the microstructure of oxide scales was investigated, which is a complementary to the previous work.
Figure 2.5 Cyclic weight gains over one thousand 1-hr cycles at 1150°C in air, showing the Si effect on oxidation behavior of co-doped $\gamma$-Ni+$\gamma'$-Ni$_3$Al alloys.

Figure 2.6 Cross sectional SEM images of oxide scale microstructures: (a) $\gamma$-Ni+$\gamma'$-Ni$_3$Al-0.05Hf-0.05Y (b) $\gamma$-Ni+$\gamma'$-Ni$_3$Al-0.1Hf-0.05Y (c) $\gamma$-Ni+$\gamma'$-Ni$_3$Al-0.1Hf-0.05Y-1Si (d) $\gamma$-Ni+$\gamma'$-Ni$_3$Al-0.05Hf-0.05Y-1Si after cyclic oxidation in Fig. 2.5
WORKS CITED


CHAPTER 3

EXPERIMENTS
There are several factors that affect the growth of oxide scales, e.g., the presence of reactive elements, grain orientation of the alloy, surface roughness, grain size. [1] In this experiment, the primary factors considered are (i) the reactive element content, (ii) oxidation time, and (iii) temperature. In order to investigate the effect of silicon on oxide growth, a series of standardized experimental procedures were designed to exclude other influential factors. Several surface analysis instruments were then used to observe the microstructures of the formed oxides.

3.1 Standardized Experimental Procedures

As is shown in Fig. 3.1, two types of samples were chosen for this experiment, Ni20Al5Cr0.05Hf0.05Y and Ni20Al5Cr0.05Hf0.05Y1Si, which allow for the investigation of silicon’s effect on oxide growth. Each sample was polished down to 0.05µm in order to achieve the same surface roughness. Subsequently EBSD was used to identify grain orientations of the alloys, and the grains whose orientation was close to <001> were investigated in further detail. Lastly, the samples were placed in a hot stage and oxidized at different temperatures and times.
3.1.1 Sample preparation of Ni-20Al-5Cr-0.05Hf-0.05Y-(1Si)

The composition of the \(\gamma/\gamma'\) two-phase alloys studied in this work is shown in Table 1. They are first produced by arc-melting high purity metals and are then cast into buttons or rods at the Materials Preparation Center of Iowa State University. A heat treatment in Ar is then conducted by Dr Brain Gleeson (University of Pittsburgh) to ensure a homogenous distribution of elements. The heat treatment procedure was as follows: homogenization at 1200°C for 6 hours, followed by a 48 hour soak at 1150°C, and then furnace cooled to room temperature.
Table 3.1 Alloy compositions used in experiments

<table>
<thead>
<tr>
<th></th>
<th>Atom%</th>
<th>Ni</th>
<th>Al</th>
<th>Cr</th>
<th>Hf</th>
<th>Y</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. γ/γ' - NiAlCrHfY</td>
<td>Bal.</td>
<td>20</td>
<td>5</td>
<td>0.05</td>
<td>0.05</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2. γ/γ' - NiAlCrHfYSi</td>
<td>Bal.</td>
<td>20</td>
<td>5</td>
<td>0.05</td>
<td>0.05</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Prior to oxidation, specimens are cut from the provided material into small plates (about 3x3x1 mm). Each side of the specimen was ground using Buehler silicon carbide paper to remove contamination. One side was then further ground with decreasing grit size in the following sequence:

\[
35\mu m \text{ (P400)} \rightarrow 22\mu m \text{ (P800)} \rightarrow 15 \mu m \text{ (P1200)} \rightarrow 9 \mu m \text{ (P2400)}
\]

Lastly, it is polished down to 0.25\(\mu m\) using diamond suspensions in the following order:

\[
3\mu m \rightarrow 1\mu m \rightarrow 0.25\mu m
\]

In order to improve the surface texture, samples for EBSD orientation mapping were further polished by a Buehler Vibramet® vibratory polisher with 0.05 \(\mu m\) Silica suspension. All specimens were cleaned in acetone and ethanol after polishing.

3.1.2 Identification of grain orientation by EBSD method

The experimental procedure is as follows: first, for any EBSD measurement, a flat and well-polished crystalline specimen is required in order to obtain a high index rate of
Kikuchi bands, and as such all samples were polished down to 0.05µm surface finish. Then, superficial marks were made using a Buehler® hardness indenter before oxidation, allowing the locations with known crystal orientation to be traced. EBSD was used to provide a crystal orientation map (with respect to Z-direction) of alloys before oxidation in air. After oxidation, FIB and SEM were used to examine the scale differences according to different crystal orientation, as well as the grain boundaries.

3.1.3 Oxidation in hot stage

Samples were placed on the TS1500 hot stage made by Linkam® before oxidation (Fig. 3.2(a)). The size of the samples should be small enough (<7mm diameter, 3mm thickness) to fit inside the chamber of the hot stage and the weight should be less than 0.1g (Fig. 3.2(b)). The hot stage is connected to a temperature controller made by Linkam® providing precise temperature and time control of various heating stages. The Type S Pt-10% Rh/Pt thermocouple in the hot stage is used to measure temperature. The temperature range for the hot stage is from ambient to 1500°C with a 130°C/min maximum heating/cooling rate. In this experiment, the samples were oxidized under three conditions: 950°C for 1min, 1150°C for 1min and 1150°C for 30min, respectively. (Figure 3.3) The samples were heated from room temperature (RT) and heated/cooled at a rate of 100°C/min back to room temperature. All oxidation experiments were performed in air.
Figure 3.2 Oxidation instruments: (a) Hot stage, (b) schematic cross section of hot stage.

Figure 3.3 Three conditions for oxidation used in the experiments.
3.2 Analytical instruments

Dual beam focused ion beam (FIB) system is a technique used for site-specific analysis, materials sputtering and deposition. The system includes a high-quality scanning electron microscope (SEM) and focused ion beam with a gallium ion source. The FIB system allows the same feature to be investigated by either an ion beam or electron beam column. However, unlike a conventional electron beam, FIB can be highly destructive to the specimen surface when a high current is applied. Therefore, one of the advantages is that the specimen can be observed by SEM when the surface material is milled away. All specimens for transmission electron microscope were prepared by two FIB work stations: a Nova Nanolab 200 and Quanta 200 3D. Each used a newly designed "lift-out" technique to prepare TEM specimens. It provides site-specific thinning at the surface of bulk material, which other techniques cannot achieve, such as electropolishing or ion milling. First, Pt is deposited on the region of interest (about 25µm* 3µm). The Pt serves to protect the surface material from being milled away by the ion beam. Then a high current ion beam is used to make two trenches at both sides of the Pt-coated area. The trenches are about 10µm deep. The thin specimen is then cut by a “U-shape” pattern, leaving a narrow “bridge” connecting to the bulk material. One edge of the specimen is then welded to the tip of a probe. After the “bridge” is cut through, the thin specimen can be transferred onto a Cu support grid. The thin specimen is thinned further down to a nano scale (~100nm) until it is transparent in TEM. In summary, FIB is used as a micro-machining tool to thin down the region of interest on the specimen.
X-ray Energy Dispersive Spectrometry (XEDS) is an analytical technique usually combined with SEM or STEM. XEDS can be used for chemical characterization of a sample. When a SEM is imaging, it emits a high-energy beam of electrons. These electrons interact with atoms in the sample and generate a range of signals including secondary electrons, characteristic X-rays, back-scattered electrons (BSE). These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample. In this work, the XEDS elemental characterizations of cross-sectional oxide scales are provided by a Libra 200FE under an accelerating voltage of 200 kV and a FEI Tecnai F30 under the acceleration voltage of 300 kV. An SEM/STEM image combined with its elemental map generated by XEDS is truly a very powerful technique. However, one difficulty of XEDS in this work relates to the deconvolution of overlapping peaks. For example, the sample Ni20Al5Cr0.05Hf0.05Y1Si contains Hf, Y, Si whose peaks are very close to each other.

<table>
<thead>
<tr>
<th>Doping Elements</th>
<th>Overlapping Peaks</th>
<th>Energy differences</th>
<th>Other peaks of Hf, Si, Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf</td>
<td>Hf (M(_\alpha)) 1.645 keV</td>
<td>Hf (M(<em>\alpha))-Si (K(</em>\alpha)): 0.095keV</td>
<td>Hf (L(_\alpha)) 7.898 keV</td>
</tr>
<tr>
<td>Si</td>
<td>Si (K(_\alpha)) 1.740keV</td>
<td>Si(K(<em>\alpha))-Y(L(</em>\alpha)): 0.182keV</td>
<td>-</td>
</tr>
<tr>
<td>Y</td>
<td>Y (L(_\alpha)) 1.922keV</td>
<td></td>
<td>Y (K(_\alpha)) 14.955keV</td>
</tr>
</tbody>
</table>

Table 3.2 Energy values of X-ray for Hf, Si and Y.

Table 3.2 shows the Hf-M\(_\alpha\) line, Si-K\(_\alpha\) line and Y-L\(_\alpha\) line lie between 1.6keV and 2.0keV, and are 1.645keV, 1.740keV, and 1.922keV respectively. The energy difference between Hf-M\(_\alpha\) line and Si-K\(_\alpha\) line is 0.095keV and the difference between Si-K\(_\alpha\) line and Y-L\(_\alpha\)-line is 0.182keV. The energy resolution of the XEDS detector on the Libra 200FE is
0.137 keV at the Mn Kα edge (5.898 keV). Theoretically, the Si Kα peak and Y Lα peak can be distinguished as two separate peaks. Moreover, we can identify Y by its Kα peak, which is 14.955 keV shown in Table 2. Unfortunately, it is impossible to separate the Hf-Mα peak and Si-Kα peak, as the energy for each peak is 1.645 keV and 1.740 keV respectively. Their energy difference is only 0.095 keV, which is smaller than the detector resolution. Although another peak of Hf (Hf-Lα), which has an energy value of 7.898 keV, is far away from Si-Kα, it cannot be used to identify Hf because the Hf-Lα peak is very close to Ni-Kα (7.477 keV) peak and Ni is the main constituent of the alloy. Another limitation of XEDS is related to the penetration depth of the electrons, when analyzing the material by a SEM equipped with X-ray spectrometers. When a beam of electrons is incident perpendicular to the sample, it results in an excitation volume within the material, which shown by Fig. 3.4. The shape of an excitation volume is jug-like with the neck of jug at the material’s surface. Obviously, the interaction volume penetrates a significant depth into the sample. The accelerating voltage and density play the largest roles in determining the depth of electron interaction. Potts [2] estimated the critical depth of electron penetration, x, as follows:

\[ x(\mu m) = \frac{0.1E_0^{1.5}}{\rho} \]  

Where, \( E_0 \) = accelerating voltage (keV) and \( \rho \) = density (g/cm³). Because the Y-Kα line is 14.955 keV, the accelerating voltage cannot be less than or equivalent to the energy value of Y-Kα line. An accelerating voltage \( E_0 = 20 \text{keV} \) is used when performing elemental mapping and point measurement. The oxide scale mainly contains Al₂O₃ (explained in
more detail in the following chapter), its density $\rho$ is no greater than $3.98 \text{ g/cm}^3$, gives $x \geq 2.25\mu\text{m}$. Since the oxide scales produced are submicron, the penetration depth of electrons is deep enough to reach the alloy when we use 20keV as the accelerating voltage of the SEM. It means a “plan view” analysis gives information not only from the oxide scale, but also from the alloy. This can bring great trouble when desiring only to focus on the oxide scale.

![Figure 3.4 Schematic shapes of electron interaction volumes](image)

**Electron backscatter diffraction (EBSD)** When an incident electron beam interacts with the material, Kikuchi bands are formed because each of the diffracting lattice planes diffract electrons differently, producing what is also called as electron backscatter diffraction pattern (EBSP). Electrons can backscatter within the material as well. When these backscattering electrons exit the crystal, they may exit by following the Bragg condition which relates to the spacing of the periodic atomic lattice planes. EBSD is
usually used for identifying the crystal orientation of the materials where the incident electron beam interacts. In this work, EBSD is conducted using a Nova Nanolab 200 equipped with the Nordlys II EBSD detector by HKL. It becomes a very powerful and useful technique when combining EBSD with FIB and SEM. It allows for comparison of the oxide scale morphology after oxidation with the grain orientation map of the parent alloy before oxidation. It also provides some evidence of the crystal orientation effect on the thermally grown oxide.

**Transmission Electron Microscopy (TEM)** can be utilized to characterize the material beyond its surface, which is much more powerful than SEM at a small scale (less than 10μm). The grain structure of the oxide was recorded in STEM mode by a High-Angle Annular Dark-Field (HAADF) detector with a long camera length. The STEM image contains diffraction contrast as well as atomic number contrast. Elemental composition of the oxide scale was analyzed by STEM in combination with the XEDS technique. In this experiment, STEM and XEDS were both performed on a FEI Tecnai F30 (300 kV) and Zeiss Libra 200FE (200 kV).
WORKS CITED


CHAPTER 4

RESULTS
It is necessary to investigate the substrate orientation effect before beginning to study the effect of silicon on the oxide scale growth. Hu et al. [1] found the effect of substrate orientation on oxidation-induced voids formation in β-NiCrAlY. According to their work, few voids were found on the grains with the crystal orientation close to <101> in the z-direction, but numerous voids were found on the grains close to <111> and <112>. Therefore, the oxide scale growth is substrate orientation-related. In order to investigate the effect of silicon on the oxide scale growth, the substrate orientation effect was excluded by selecting certain grains (<001> in z direction) on both NiAlCrHfY and NiAlCrHfYSi. Then, after being oxidized in a series of oxidation conditions, the oxide scales formed on NiAlCrHfY and NiAlCrHfYSi were compared in this study.

4.1. The substrate orientation effect on the oxide scale growth

Both NiAlCrHfY and NiAlCrHfYSi were studied in this section. Prior to oxidation, the samples were polished down to 0.05μm and cleaned in order to decrease their surface roughness. Then the crystallographic orientation of the grains normal to the plane of the sample (z-direction) was examined by EBSD mapping. As is shown in Fig 4.1(a), a stereographic triangle is a color key of the inverse pole figure map for Fig 4.1 (b), where each color represents a certain grain orientation. Here we choose the z-axis as its physical direction to plot the inverse pole figure map. For example, grains with the orientation of <001> in the z-axis are marked red, those with <101> direction in z-axis are marked green, and grains with the orientation of <111> in z-axis are marked blue. Those grains having other orientations are marked between red, green and blue. The grain boundaries can be identified due to the color differences in the orientation map. In Fig 4.1
(b), the unindexed pixels, which are shown by black arrows, represent three superficial hardness indenter marks. These marks, as well as grain boundaries, were used to trace the grains with known crystal orientation after oxidation. In Fig 4.1 (b), two individual grains are indicated as G1 and G2. The orientation of G1, G2 can be identified by the stereographic triangle in Fig 4.1(a). The orientation of G1 is therefore close to <001> and that of G2 is close to <101>. Grains close to the orientation G3 <111> have not yet been found on NiAlCrHfY in this work.

After oxidation at 1150°C for 1min in air, a plan view secondary electron (SE) image (Fig4.1 (c)) was recorded at the black rectangle in Fig4.1 (b). In Fig 4.1(c), different surface morphologies on G1 and G2 could be observed directly. The growth of “second generation” [2] oxide nodules (1~4µm diameter) occurred randomly both in G1 and G2. However, the yellow rectangle in Fig. 4.1(c) shows many more submicron nodules (diameter less than 0.5µm) formed on G2, relative to that grown on G1. These small oxide nodules agglomerate preferentially along micro scratches and the grain boundaries. In the next section, the STEM-EDS elemental maps show that the submicron nodules are Ni-rich oxides, which grow rapidly during the early stages of oxidation.
Figure 4.1. NiAlCrHfY: (a) stereographic triangle, which is the color key for image (b); (b) EBSD inverse pole figure (IPF) map of grains normal to the plane, two individual grains are indicated as G1 and G2; (c) SEM plan view of the oxide after oxidation in 1150°C for 1min in air; fewer submicron nodules were found on G1 (Z close to <001>) relative to G2.
This finding is confirmed by the investigation of the sample NiAlCrHfYSi which has 1 at. % of silicon addition. Prior to oxidation, the sample NiAlCrHfYSi was prepared in the same way as described above and the crystallographic orientation of grains normal to the plane of the sample was examined by EBSD (Fig.4.2). As is shown in the black frame in Fig. 4.2(b), three grains, G1, G2, G3, whose orientation are close to <001>, <101>, <111>, respectively, merged at a triple point. After oxidation at 1150°C for 1min, the region in the black frame was studied by SEM (Fig. 4.2(c), (d)). The SEM images in Fig. 4.2(c), (d) showed the sample that was recorded under different accelerating voltages: 5KV is used in Fig. 4.2(c) and 15KV is used in Fig. 4.2(d). Different accelerating voltages of the electron beam provide different information of the sample as the voltage influences the penetration depth of the electron beam. When using 5KV as the accelerating voltage, the penetration depth in Al₂O₃ is about 0.3µm according to Potts’s equation (mentioned in Chapter 3). Therefore, its SE image reflects mainly surface topography of the sample. As is shown in Fig. 4.2(c), the submicron-size nodules agglomerated in the grain G2, especially at grain boundaries and surface depressions. Few Ni-rich nodules can be found in the grain G1 and even fewer Ni-rich nodules can be found in the grain G3. However, the hole-like structures at the interface between the oxide and alloy are not visible under this condition. When using 15KV as the accelerating voltage, the penetration depth is about 1.5µm and the SE image mainly reflects mass density difference. In Fig. 4.2 (d), the hole-like structures at the oxide/alloy interface, which were shown by the green arrows, are visible due to the high accelerating voltage.

In order to exclude the substrate orientation effect on oxidation, we selected the grains close to <001> to investigate the Si effect on oxidation in this study. Fig.4.3
displays a cross sectional SE image of oxides scales grown on the substrates with the grain orientation close to \langle001\rangle. Much more Ni-rich oxide (the layer with light contrast shown by blue arrows) formed on NiAlCrHfY than on NiAlCrHfYSi, which has been proven by the STEM-EDS elemental mapping in the following section. Also, much more interfacial voids can be found within the oxide scale of NiAlCrHfY than that in NiAlCrHfYSi.
Figure 4.2 NiAlCrHfYSi: (a) stereographic triangle as the color key for (b); (b) EBSD inverse pole figure (IPF) map of grains normal to the plane, a rectangle region (black frame) contains three individual grains indicated as G1 (<001>-orientated), G2 (<101>-orientated) and G3 (<111>-orientated); (c) SE plan view image of the oxide after oxidation in 1150°C for 1 min, less Ni-rich oxide was found on G3; SE image was taken under an accelerating voltage of 5kV. (d) SE image was taken at the same region of that shown in (c), but under an accelerating voltage of 15kV.
Figure 4.3 Cross-sectional SEM image of alloys with the grain orientation close to <001> after oxidation at 1150°C for 1 min: (a) NiAlCrHfY (b) NiAlCrHfYSi.
4.2 Oxidation of NiAlCrHfY(Si) at 950°C for 1 min

In order to investigate the Si effect on the growth of the oxide scale, the alloys were oxidized at different temperatures for different times. The alloys are divided into three groups and each group includes two types of samples: NiAlCrHfYSi and NiAlCrHfY. Each was heated under three different oxidation conditions — 950°C for 1 min, 1150°C for 1 min and 1150°C for 30 min. In Condition 1, after oxidation at 950°C for 1 min, a thin oxide film grew on the sample surface. There are some differences in the oxide scales between the alloys with and without Si doping. According to the STEM-EDS elemental mapping in Fig.4.4, the alloy without Si doping formed an outer NiO layer, an inner continuous Al₂O₃ layer and much Cr₂O₃ within the scale. The layer above the oxide scale, which is orange in the EDS map, represents the deposition of platinum, which protects the surface materials from being milled away by the ion beam. However, according to Fig.4.5, the oxide scale of the alloy with Si doping only consists of a single layer of Al₂O₃ with some Cr-containing oxide particles. Therefore, the addition of Si helps to form an outer continuous Al₂O₃ layer on NiAlCrHfYSi after oxidation at 950°C for 1 min. The minor elements (Hf, Y, Si) were not found in the oxide scale by STEM-EDS due to the low intensities of these elements.

4.3 Oxidation of NiAlCrHfY(Si) at 1150°C for 1 min

In Condition 2, alloys were oxidized at 1150°C for 1 min, STEM-EDX elemental maps (Fig.4.6) showed the oxide scale formed in the alloy without Si doping; it is shown to consist of an outer NiO layer, the middle spinel (NiAl₂O₄) and Cr-rich oxides (Cr₂O₃/
NiCr$_2$O$_4$) and an inner Al$_2$O$_3$ layer. In the alloy with Si doping, a thicker Al$_2$O$_3$ layer formed after oxidized at 1150°C for 1 min (Fig.4.7). The Ni content was higher in the outer part of the Al$_2$O$_3$ scale relative to that in the inner part of Al$_2$O$_3$ scale. The Cr-containing oxides (Cr$_2$O$_3$ and/or NiCr$_2$O$_4$) formed in the inner part of the Al$_2$O$_3$ scale. In Figure 4.5, voids at the oxide/alloy interface formed due to the “Kirkendall effect”, [3] which were explained in further detail.
Figure 4.4 Cross-sectional STEM-EDX elemental maps of NiAlCrHfY oxidized at 950°C for 1 minute, showing the oxide scale consists of an outer NiO layer, an inner Al₂O₃ scale and Cr-containing oxide within the scale.
Figure 4.5. Cross-sectional STEM-EDX elemental maps of NiAlCrHfYSi oxidized at 950°C for 1 minute, showing the oxide scale consists of an single Al₂O₃ scale and Cr-containing particles in the inner part of the Al₂O₃ scale.
Figure 4.6 Cross-sectional STEM-EDX elemental maps of NiAlCrHfY oxidized at 1150°C for 1 minute, showing the oxide scale consists of the top NiO, the middle Ni(Cr,Al)\textsubscript{2}O\textsubscript{4}/Cr\textsubscript{2}O\textsubscript{3} and the inner most Al\textsubscript{2}O\textsubscript{3}.
Figure 4.7 Cross-sectional STEM image and its EDS elemental maps of NiAlCrHfYSi oxidized at 1150°C for 1 min, revealing the oxide scale mainly consists of a single Al₂O₃ scale, which includes higher Ni content in the outer part of the Al₂O₃ scale and higher Cr content at the inner part of the Al₂O₃ scale.
4.4 Oxidation of NiAlCrHfY(Si) at 1150°C for 30 min

In Condition 3, the alloy NiAlCrHfY was oxidized at 1150°C for 30 min in air. In Fig. 4.8, the STEM-EDS maps indicate the oxide scale of NiAlCrHfY mainly consists of two layers: the outer NiO/NiAl\(_2\)O\(_4\) spinel, and an inner Al\(_2\)O\(_3\) layer. Some Cr\(_2\)O\(_3\) and/or NiCr\(_2\)O\(_4\) exist at the interface of the Ni rich layer and the Al rich scale. However, the difference of the oxygen signal in the O map is mostly due to the thickness variation of the TEM specimen. The STEM image in Fig. 4.9 shows that the oxide scale of NiAlCrHfY contains many voids at the interface of NiO/spinel and Al\(_2\)O\(_3\). In Table 4.1, elemental quantitative analysis provides the atomic percentages of elements that are contained in the oxide scale. The elemental contents at Area 1 and Area 2 are nearly identical and the ratio of Ni: Al: O is close to 1:2:4, which is close to the ratio of NiAl\(_2\)O\(_4\) spinel. At Area 4 and Area 5, the ratio of Al to O is close to 2:3 and the atomic percentage of Ni is less than 1%. Therefore, the main content at Area4 and Area5 is probably Al\(_2\)O\(_3\). The Area 3, which is at the interface of NiO/spinel and Al\(_2\)O\(_3\), has a ratio of Ni: Al :O close to 1: 3: 5.5. Leading to the conclusion that Area 3 probably contains a mixture of Al\(_2\)O\(_3\), NiO and spinel.

A much thicker single Al\(_2\)O\(_3\) scale formed when NiAlCrHfYSi was oxidized at 1150°C for 30 minutes in air. As is shown in Fig. 4.10, the top two layers A and B represent the depositions of Pt and Pd before TEM sample preparation, in order to protect the surface oxides from being damaged and increase the surface conductivity. According to the STEM-EDS maps in Fig. 4.11, the oxide scale below Pd deposition was mostly Al\(_2\)O\(_3\). The Cr-rich oxide, which we observed in Fig. 4.7 was absent in the elemental
maps in Fig. 4.11 after oxidation at 1150°C for 30 min. The Cr-rich oxide probably spread out in the Al₂O₃ scale and the dilute content of Cr may be difficult to be detected in the elemental maps. A relatively high Ni content was contained in the outer part of the Al₂O₃ scale. Submicron size Ni-rich precipitates were embedded at the inner part of the Al₂O₃ scale.

Table 4.2 shows the EDS quantitative analysis results of the particles and their surrounding oxides in red circles in Fig. 4.10. Area 1 and Area 2 are selected in the outer part of the scale, which contain 1%~2% Ni where the ratio of O to Al is very close to Al₂O₃. Area 3 and 4 located on two precipitates that have higher contrast in the STEM image, reveal about 10% Ni is contained in the precipitates according to the results in Table 4.2. Area 5 and 6 is at the inner part of the oxide scale. The atomic percentages of Ni content at Area 5, 6 are 0.1% and 0.2%, respectively. The O to Al atomic ratios of the Area 3, 4, 5, 6 are 0.7, 0.8, 1.6, 1.5, respectively. The O to Al atomic ratio of the precipitates is less than 1 while the ratio of their surrounding oxides is close to 1.5, which is the ratio of Al₂O₃. It reveals that the precipitates with higher contrast are most likely metallic Ni. Less Ni is oxidized to NiO/ spinel and Ni must diffuse to the outer part of the scale in NiAlCrHfYSi. Hf and Y can hardly be found through the Al₂O₃ scale of NiAlCrHfYSi. There are two possibilities for the absence of Hf and Y according to the results of EDS analysis: one is the oxide scale at this region does not contain any Hf or Y, the other is the distribution of Hf and Y is homogeneous through the oxide scale. The average contents for Hf and Y in the bulk material are about 0.05 at.%; it is impossible for XEDS detector to identify the Hf and Y if their contents are as low as those in the bulk material.
Figure 4.8. Cross-sectional STEM-EDX elemental maps of NiAlCrHfY oxidized at 1150°C for 30 minutes, revealing that the oxide scale consists of an outer NiO/spinel, an inner Al₂O₃ scale with some Cr₂O₃/spinel inside.
Figure 4.9 Cross-sectional STEM image of NiAlCrHfY oxidized at 1150°C for 30 minutes; elemental quantitative analysis on Area 1, 2, 3, 4, 5 has done by XEDS and are marked by blue rectangles.

<table>
<thead>
<tr>
<th></th>
<th>Area 1</th>
<th>Area 2</th>
<th>Area 3</th>
<th>Area 4</th>
<th>Area 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>50.2</td>
<td>52.3</td>
<td>56.0</td>
<td>63.6</td>
<td>57.8</td>
</tr>
<tr>
<td>Al</td>
<td>32.8</td>
<td>32.4</td>
<td>33.3</td>
<td>35.8</td>
<td>40.2</td>
</tr>
<tr>
<td>Ni</td>
<td>16.7</td>
<td>15.0</td>
<td>10.5</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Cr</td>
<td>0.3</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 4.1 Atomic percentages of O, Al, Ni, Cr at Areas 1, 2, 3, 4 and 5 from Fig. 4.9.
Figure 4.10. STEM image of cross-sectional oxide scale on NiAlCrHfYSi after heating at 1150°C for 30 minutes in air. (A) Pt deposition, (B) Pd deposition, (C) the oxide scale (mostly Al₂O₃), (D) substrate alloy. Elemental quantitative analysis on Area 1, 2, 3, 4, 5, 6 has been performed by XEDS, which are marked by red circles.
Figure 4.11 Cross-sectional STEM-EDX elemental maps of NiAlCrHfYSi oxidized at 1150°C for 30 minutes, revealing that the oxide scale mainly consists of a single Al$_2$O$_3$ scale and some nano-size Ni-rich particles are embedded at the inner part of the Al$_2$O$_3$ scale.
### Table 4.2 Atomic percentages of contained elements at Areas 1, 2, 3, 4, 5, 6 from Fig. 4.10.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>56.5</td>
<td>56.6</td>
<td>36.9</td>
<td>38.0</td>
<td>60.3</td>
<td>60.1</td>
</tr>
<tr>
<td>Al</td>
<td>41.8</td>
<td>40.7</td>
<td>52.7</td>
<td>52.2</td>
<td>38.9</td>
<td>37.2</td>
</tr>
<tr>
<td>Ni</td>
<td>1.2</td>
<td>2.1</td>
<td>10.2</td>
<td>9.4</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Cr</td>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
<td>0.3</td>
<td>0.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Si</td>
<td>0.3</td>
<td>0.4</td>
<td>-</td>
<td>0.1</td>
<td>0.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Hf</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Y</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
WORKS CITED


5.1 Evolution in the chemistry and microstructure of the oxide scale

As was mentioned earlier, during the initial oxidation experiment, 950°C for 1 min, the oxide scale of Ni-20Al-5Cr-0.05Hf-0.05Y consists of an outer NiO layer, the middle Cr₂O₃ and an inner Al₂O₃ layer (Fig.4.4). The oxide scale of Ni-20Al-5Cr-0.05Hf-0.05Y-1Si consists only of a single layer of Al₂O₃ (Fig.4.5). Reactions [1] that took place in the oxide scale and the oxide/ alloy interface can be written as Eqns. (1), (2) and (3). When the alloys were heated at 1150°C for 30 min, the outer NiO layer that initially formed on Ni-20Al-5Cr-0.05Hf-0.05Y converted to Ni(Al,Cr)₂O₄ spinel (Fig.4.9). The related solid-state reactions are interpreted by Eqn. (4) and (5). Phillips et al. [4] indicated that once the external NiO/ spinel formed, it remained in the scale during further oxidation due to the poor solubility of NiO/ spinel in both Cr₂O₃ and Al₂O₃. The NiO/spinel remains upper most scale of Ni-20Al-5Cr-0.05Hf-0.05Y after oxidation at 1150°C for 30 min, which agrees with Phillips’s statement. The oxide scale of Ni-20Al-5Cr-0.05Hf-0.05Y-1Si consisted of a layer of Al₂O₃ that contained a relatively high Ni content in the outer part of the Al₂O₃ scale (Fig.4.11).

\[ Ni + \frac{1}{2}O_2 = NiO \] (1)

\[ 2Cr + \frac{3}{2}O_2 = Cr_2O_3 \] (2)

\[ NiO + Cr_2O_3 = NiCr_2O_4 \] (4)

\[ NiO + Al_2O_3 = NiAl_2O_4 \] (5)

\[ 2Al + \frac{3}{2}O_2 = Al_2O_3 \] (3)
Young [2] reported that the thermal stability decreased in this sequence: $\text{Al}_2\text{O}_3$ > $\text{Cr}_2\text{O}_3$ > NiO in the temperature range of interest. Therefore, NiO is expected to form rapidly as the top scale. The equilibrium oxygen partial pressure at the interfaces (I) NiO/spinel)/Cr$_2$O$_3$, (II) Cr$_2$O$_3$/Al$_2$O$_3$, (III) Al$_2$O$_3$/alloy decreases in this sequence $P_{\text{O}_2}(\text{I}) > P_{\text{O}_2}(\text{II}) > P_{\text{O}_2}(\text{III})$, under the assumption that all metals have unit activity. However, Nijdam et al. [3] suggested that other factors, e.g. the presence of reactive elements, would also influence the formation of the oxide scale in addition to thermodynamics. According to the observation in our study, the addition of Si promotes the preferential formation of Al$_2$O$_3$ on Ni-20Al-5Cr-0.05Hf-0.05Y-1Si both at 950°C and 1150°C. This will be discussed in further detail.

Ni-rich precipitates were found in the inner part of the Al$_2$O$_3$ scale formed on Ni-20Al-5Cr-0.05Hf-0.05Y-1Si after 30 min of oxidation (Fig.4.11). Molins and Hou et al. [4] reported that after 1 hour of oxidation at 1100°C, Ni-rich precipitates were widely distributed throughout the Al$_2$O$_3$ scale formed on β-Ni-40Al. Hayashi and Gleeson [5] also reported that the Ni-rich precipitates were found only in the inner part of the Al$_2$O$_3$ scale formed on Pt-modified γ’-Ni$_3$Al alloys with and without Hf addition after 10 min of heating at 1150°C. Moreover, according to our study and Hayashi’s study, the Ni content was relatively high in the outer part of the Al$_2$O$_3$ scale, but nearly no Ni content was found in the vicinity of the Ni-rich precipitates. It is believed that during the oxidation reaction, the local oxygen partial pressure decreased because of the progressive growth of Al$_2$O$_3$, which would, in turn, lead to the supersaturation of Ni, especially in the inner part of the Al$_2$O$_3$ scale. Eventually, this supersaturation would result in the precipitation of Ni-rich metallic particles. [5] At 1000°C, the Ni-Al-O phase diagram reported by Elrefaie
et al. [6] showed that the Ni solubility in Al$_2$O$_3$ decreased with decreasing oxygen pressure (Fig. 5.1). Hence, the Ni-rich metallic particles would be rejected and oxidized in the outer part of the Al$_2$O$_3$ scale. In Table 4.2, the EDS quantitative analysis also shows the oxygen and aluminum contents decreased in these precipitates. The size of the precipitates is no larger than 40nm, whereas the thickness of the TEM specimens is about 150nm. Therefore, the Ni-rich precipitates were completely embedded in the Al$_2$O$_3$ scale and the strong signal of O and Al from Al$_2$O$_3$ would affect the quantitative analysis of the precipitates.

After 30 min of oxidation at 1150°C, Cr$_2$O$_3$/NiCr$_2$O$_4$ have not been found in the oxide scale of Ni-20Al-5Cr-0.05Hf-0.05Y-1Si, which existed in the oxide scale when Ni-20Al-5Cr-0.05Hf-0.05Y-1Si was oxidized at 950°C and 1150°C for 1 min. The Cr-rich oxide probably spread out in the Al$_2$O$_3$ scale and the dilute content of Cr may be difficult to detect by XEDS. Representing a summary of the oxidation data found in our study, a schematic diagram was plotted to show the evolution of layered oxides on $\gamma/\gamma'$-NiAlCrHfY(Si) alloys (Fig.5.2.). Ni-20Al-5Cr-0.05Hf-0.05Y-1Si tend to form a relatively pure Al$_2$O$_3$ scale compared to the scale formed on Ni-20Al-5Cr-0.05Hf-0.05Y under the three oxidation conditions: 950°C for 1min, 1150°C for 1min and 1150°C for 30min. The thickness of the oxide scale formed on the two alloys with and without Si addition is almost the same.
Figure 5.1 The phase diagram of Ni-Al-O at 1000°C proposed by Elrefaie.
Figure 5.2 Schematic diagram of the evolution of layered oxides formed on $\gamma/\gamma'$-NiAlCrHfY(Si) alloys.
5.2 Effect of Si on the evolution of layered oxide

There are three primary positive effects of reactive elements on the oxidation of NiAlCr alloys reported by Moon [7]: (a) promote the selective oxidation of stable oxides with low diffusivities, such as Al₂O₃ and Cr₂O₃; (b) reduce the growth rate of NiO and Cr₂O₃ scales; (c) increase the scale adherence on both Al₂O₃- and Cr₂O₃-forming alloys. The scale differences between the two alloys NiAlCrHfY and NiAlCrHfYSi are (1) fewer and smaller voids formed within the oxide scale on NiAlCrHfYSi and (2) the formation of NiO/spinel is reduced on NiAlCrHfYSi. The observations in our study are in excellent agreement with Moon’s statement on the positive effects of reactive elements mentioned above.

As the Al₂O₃ scale grows, the depletion of Al occurs in the alloy close to the oxide/ alloy interface, which results in the excess of Ni in this area. The Ni atoms will then diffuse inwards in order to balance the Ni content in the entire alloy. [12] In an Al-deficient zone, the Ni inward diffusion is much faster than the Al outward diffusion. Therefore, a net flux of vacancies diffuses outwards from the interior to the oxide/ alloy interface to compensate for the Ni inward diffusion. The vacancies then agglomerate and form so-called “Kirkendall voids” within the scale and at the oxide/ alloy interface. [13] In this study, no evidence was found that the addition of Si could reduce the void formation at the oxide/ alloy interface.

There is a limitation for the STEM-XEDS technique that the minor elements (Hf, Y, Si) are difficult to detect due to the peak convolution and the low intensities of these elements in the oxide scale. Some previous work related to the oxidations of Ni-20Al-
5Cr-0.05Hf-0.05Y-(1Si) has been done by Hovis (Case Western Reserve University). Figure 5.3 shows TOF-SIMS elemental maps for the oxide scales of the alloys heated at 1100°C for 50 min in air provided by Hovis. The intensities of Hf and Y represent an average through the entire oxide scale. Fig5.3 (a) and (b) are the intensities of Hf and Y from the oxide scale of Ni-20Al-5Cr-0.05Hf-0.05Y, respectively. Hf and Y tend to agglomerate together, and the distributions of Hf and Y are not homogeneous through the oxide scale. Fig.5.2 (c) and (d) are the intensities of Hf and Y from the oxide scale on Ni-20Al-5Cr-0.05Hf-0.05Y-1Si, respectively. It is well known that Hf and Y distribute along the grain boundaries of Al₂O₃, which has small grain sizes (about 0.5~2μm). [11] According to the TOF-SIMS maps, which have a scale bar of 100μm, the distributions of Hf and Y are homogeneous along the grain boundaries. According to the observations of Hovis, the addition of Si helps to redistribute Hf and Y homogeneously throughout the oxide scale. However, the mechanism for redistribution of Hf and Y by the addition of Si to the bond coat is not clear.
Figure 5.3 Elemental maps by TOF-SIMSI, alloys were heated at 1100°C for 50min in air: a) Hf intensity from the oxide scale of NiAlCrHfY; b) Y intensity from the oxide scale of NiAlCrHfY; c) Hf intensity from the oxide scale of NiAlCrHfYSi; d) Y intensity from the oxide scale of NiAlCrHfYSi.
WORKS CITED


(2004), pp 231-238.

CONCLUSION

1. Crystal orientation identification by EBSD combined with a STEM imaging technique has shown that the grain orientation of the alloys influence the oxide formation on the NiAlCrHfY(Si). During the early stages of oxidation, grains close to <001> have much less NiO/spinel formation and fewer voids at the NiO (spinel)/Al₂O₃ interface, relative to the oxides formed on grains close to <101> or <111>. In order to exclude the effect of grain orientation, only the grains of NiAlCrHfY(Si) close to <001> were chosen to be studied in this work.

2. The microstructures of oxide scale formed on selected grains of NiAlCrHfY(Si) were compared to determine the effect of 1 at.% of Si on the scale evolution of the alloys. NiAlCrHfY formed an external NiO/spinel scale and an internal Al₂O₃ scale, with some internal voids and Cr₂O₃/NiCr₂O₄. NiAlCrHfYSi formed a single Al₂O₃ scale, which consisted of a small amount of Ni content in the outer part and Ni-rich particles at the inner part. The outward diffused Ni-rich particles found in Al₂O₃ scale contribute to the formation of top NiO/spinel scale. As the oxidation time increasing, the initially formed Cr₂O₃/ spinel in the oxide scale most likely spreads out in the Al₂O₃ scale, but the dilute content of Cr is difficult to detected by the XEDS detector.

3. The addition of Silicon promotes the formation of a scale with less NiO/spinel and fewer voids at the NiO (spinel)/Al₂O₃ interface due to its beneficial effect on decreasing the outward diffusion of Ni from the alloy. However, no evidence was
found in our study that the addition of Si could reduce the void formation at the oxide/ alloy interface.
FUTURE WORK

In this work, the beneficial effect of Si on decreasing the formation of NiO/ Ni(Cr,Al)$_2$O$_4$ is considered to be due to the redistribution of Hf and Y, according to Hovis’s experimental observation by TOF-SIMS mapping. However, the mechanism for the effect of the minor elements (Hf, Y, Si) on the outward diffusion of Ni is not clear. So, the future work should aim at finding the mechanism for the reduction of NiO formation due to the addition of Si and the mechanism for redistribution of Hf and Y by the addition of Si to the bond coat.

1. Oxidation experiments at a lower temperature $T$ ($750^\circ$C<$T$ > 950$^\circ$C) for a shorter heating time $t$ ($t< 1$ minute) should be conducted in future work in order to investigate the thin oxide film (several nanometer thickness) that initially forms on the NiAlCrHfY(Si). STEM-EDS as well as other techniques such as X-ray photoelectron spectroscopy should be used to identify the major elemental compositions (Ni, Al, Cr) of the thin oxide film.

2. In this study, STEM-EDS has proven that it is difficult to identify the small amount of Hf, Y and Si in the oxide scale due to the peak convolution and low intensity. Other state-of-the-art analytical techniques, such as Local-Electrode Atom-Probe (LEAP) tomography should be conducted on a thinner oxide film.
Appendix I: Distribution of Hf and Y at the oxide scale of the alloy

The addition of Si is considered to redistribute Hf and Y, which has been discussed in Chapter 5. The STEM-EDS quantitative analysis on NiAlCrHfYSi revealed that the nano-size particles with higher contrast are probably metallic Ni supersaturated from the Al₂O₃ scale. Hf and Y can hardly be found either in the particles or in the vicinity of the Ni-rich particles of NiAlCrHfYSi. There are two possibilities for the absence of Hf and Y in the EDS maps: one is the oxide scale at this region does not contain any Hf or Y, the other is the distribution of Hf and Y is homogeneous through the oxide scale. The average contents of Hf and Y in the bulk material are 0.05 at.%; it is impossible for the XEDS detector to identify the Hf and Y if their contents are also less than 1 at.%. The TOF-SIMS maps provided by Hovis supported the second explanation for the absence of Hf and Y in the EDS maps.

According to the STEM-EDS, higher intensities of Hf and Y have been found in NiAlCrHfY that was oxidized at 1150°C for 30 mins. In FigI-1, a cross sectional STEM image shows the oxide scale of NiAlCrHfY, which contains some particles with higher contrast. Two X-ray energy dispersive spectrums (Area 1 and 3 in Fig. I-1(b)) were plotted for comparison. Area 1 was centered on a particle and its spectrum is shown in yellow. Area 3 was on the surrounding oxide that was selected for comparison and its spectrum was shown by the red line in Fig. I-1(b). Two white arrows indicate that the spectrum of Area 1 has an extra “shoulder” at 7.898keV and a separate peak at 1.645keV, which are the Hf -Lα peak and the Mα peak, respectively. So Area 1 has a much higher counts for Hf relative to that of Area 3. In Fig I-1 (c) The spectrum was acquired from
another particle at Area 2, which was shown in Fig. I-1 (a). A small Y-Lα peak appeared on the spectrum, which indicated that Y is contained in the particle in Area 2. XEDS quantitative analysis in Table I-1 showed the elemental contents at Area 1, 2 and 3. At the lower part of the scale, the oxide is mostly Al₂O₃. Moreover, some particles are embedded in Al₂O₃, which contains relatively high Hf (2.4 at. % in Area1) and Y (0.5 at. % in Area 2) concentration compared to the average concentrations in the bulk material (0.05 at. %) before oxidation. In conclusion, Hf and Y agglomerated as nano-size particles in the oxide scale of NiAlCrHfY after being heated at 1150°C for 30 mins.
Figure I-1. NiAlCrHfY oxidized at 1150°C for 30 mins in air: (a) Cross-sectional STEM image on the oxide scale; Small particles (Area 1,2) with high contrast are observed in the oxide scale; (b) the XED spectrums of Area 1 and 3 were indicated by yellow area and red line, respectively; (c) the XED spectrum for Area 2.
<table>
<thead>
<tr>
<th></th>
<th>Area 1</th>
<th>Area 2</th>
<th>Area 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>58.4</td>
<td>60.3</td>
<td>58.4</td>
</tr>
<tr>
<td>Al</td>
<td>34.5</td>
<td>32.9</td>
<td>39.7</td>
</tr>
<tr>
<td>Ni</td>
<td>4.4</td>
<td>5.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Cr</td>
<td>0.3</td>
<td>0.6</td>
<td>1.5</td>
</tr>
<tr>
<td>Hf</td>
<td>2.4</td>
<td>0.9</td>
<td>-</td>
</tr>
<tr>
<td>Y</td>
<td>-</td>
<td>0.5</td>
<td>-</td>
</tr>
</tbody>
</table>

Table I-1 Atomic percentages of the elements contained at Areas 1, 2, 3, 4 and 5 from Fig.I-1.
Appendix II: Surface morphologies of the TGO

Before oxidation, the distribution of Y is not homogeneous in the NiAlCrHfY(Si) bond coat alloys, due to the low solubility of Y in the alloys. In Figure II-1, the agglomerated Y-rich particles (about 0.5μm~2.5μm) exhibited higher intensity of the back-scattered electrons (BSE) signal than the NiAlCrHfYSi substrate alloy. EDX measurements revealed that about 10 at. % to 11 at. % of Y is contained within these particles. After oxidation, those Y-rich particles were oxidized and formed micron-sized nodules on the TGO surface.

As is shown in Figure II-2, the blue arrows in the SEM images showed the growth of micron-sized nodules on the surface of two alloys after oxidation at 1150°C for 1min. The micron-sized nodules distributed randomly on grains and grain boundaries. In Figure II-3, two SEM images were from the same samples as those shown in Figure II-2, but they were in higher magnification. In Figure II-3, the samples were tilted to 52° in order to give a better view of the oxides. In addition, different shapes of the micron-size nodules formed on different alloys (with and without Si doping). Most of the nodules formed on NiAlCrHfYSi are ring-shaped, which look like “bagels”; while the nodules formed on NiAlCrHfY are semi-sphere shaped. The cross-sectional view of a FIB cut on one of the nodules formed on NiAlCrHfYSi was shown in Figure II-4. According to the SEM-EDS maps in Figure II-4, Ni-rich oxide lied above the surrounding TGO surface. An underneath oxide peg consists of the Y-rich oxide cluster, a middle layer of Cr-rich oxide and an inner layer of Al₂O₃. The layer of Al₂O₃ lied at the interface of the oxide peg.
and the alloy, which protected the alloy from inner oxidation. Voids formed inside the oxide scale and at the interface of oxide/alloy.
Figure II-1. Backscattered electron (BSE) image of NiAlCrHfYSi before oxidation.

Figure II-2. 0° tilted SEM images with lower magnification showed the surface morphologies of (a) NiAlCrHfY, (b) NiAlCrHfYSi after oxidation at 1150°C for 1min.
Figure II-3. 52° tilted SEM images showed the surface morphologies after oxidation at 1150°C for 1min: (a) NiAlCrHfY, (b) NiAlCrHfYSi.

Figure II-4. STEM-EDX elemental maps of the micron-size nodules formed on NiAlCrHfYSi after oxidation at 1150°C for 1min.
Appendix III: Distribution of Hf and Y at grain boundaries of the alloy

The oxidation behaviors we have mentioned above are all related to the bulk grains of the alloy. STEM-EDS analysis of the cross-sectional NiAlCrHfY revealed the preferential oxidation along the grain boundaries of the alloys (Fig. III-1). In Fig.III-1(a), the yellow frame on the cross-sectional STEM image reveals the region where the EDX line-scan analysis was performed. In Fig.III-1(c), EDX line-scan reveals that the oxygen has diffused preferentially along the grain boundaries down to several microns, while the oxides formed on the surface of bulk grains is about one micron thick. The dominant content at the grain boundaries is Y, which is shown by the dark red peak in Fig. III-1(c). Two Hf peaks that are indicated by green color can be found at the two edges of the Y peak. In Fig.III-1(b), the STEM image taken by the HAADF detector with short camera length shows the higher contrast at the grain boundary contained heavy elements. The curves of the elemental intensities for Hf and Y superimposed onto the STEM image show that Hf is segregated at the grain boundaries of the NiAlCrHfY. Almost identical results have been observed at the grain boundary of alloy NiAlCrHfYSi except for the distribution of Hf. The dark red line, blue line and bright red line in the EDX line-scan (Fig. III-2(b).) indicates the count variations of Y, Si and O along the signal-acquiring direction (yellow arrow) in Fig. III-2 (a). These three elements have higher counts at the grain boundary of the NiAlCrHfYSi alloy. However, there is no significant variation for the counts of Hf between the bulk alloy and the grain boundary. In addition, the counts of Ni, Al and Cr decreased at the grain boundary. In conclusion, the solubility of reactive elements (Hf, Y) is very low at the bulk alloy, which usually distributed at the grain
boundaries of the bulk alloy. However, the addition of Si seems to redistribute Hf and decrease the Hf content in the grain boundaries.
Figure III-1. (a) Cross-sectional STEM image of the oxide scale and the grain boundary of NiAlCrHfY after heating at 1150°C for 1min in air. (b) STEM image of the yellow frame with higher magnification than (a). EDX line-scan across the grain boundary of the bulk material, the dark red line and green line indicate the content variations of Y and Hf, respectively. (c) EDX line-scan along the yellow arrow in (b).
Figure III-2. (a) STEM image of cross-sectional NiAlCrHfYSi on the grain boundary after heating at 1150°C for 1min. (b) EDX line-scan along the yellow arrow in (a)
BIBLIOGRAPHY


A. Atkinson: The Institute of metals. 1988, 1046-1051


C. Wagner, Zeitschrift Fur Electrochem, 63, 772(1959)


D.P.Moon: Materials Science and Technology Vol. 5, 754-764, 1989


