The reactive element effect of yttrium and yttrium silicon on high temperature oxidation of NiCrAl coating

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Abstract. The microstructure formed on the bond coat affects the oxidation resistance, particularly the formation of a protective oxide layer. The adhesion of bond coat and TGO increase significantly by addition of reactive element. In the present work, the effect of yttrium and yttrium silicon as reactive element (RE) on NiCrAl coating was investigated. The NiCrAl (without RE) and NiCrAlX (X:Y or YSi) bond coating were deposited on Hastelloy C-276 substrate by High Velocity Oxygen Fuel (HVOF) method. Isothermal oxidation was carried out at 1000 ⁰C for 100 hours. The results showed that the addition of RE could prevent the breakaway oxidation. Therefore, the coating with reactive element were more protective against high temperature oxidation. Furthermore, the oxidation rate of NiCrAlY coating was lower than NiCrAlYSi coating with the total mass change was ±2.394 mg/cm² after 100 hours of oxidation. The thickness of oxide scale was approximately 1.18 μm consisting of duplex oxide scale of spinel NiCr₂O₄ in outer scale and protective α-Al₂O₃ in inner scale.

1. Introduction
Hastelloy X as a common Ni based superalloy is mostly used in gas turbines that operate at elevated temperature. Ni-based superalloy substrate has good mechanical properties at high temperature. The microstructure superalloy composes of high stable austenite containing significant amounts of alloying elements such as Cr, Mo, Al, Ti, Fe, and C [1]. It is well known that coating on the surface of Ni-based superalloy is required to improve the oxidation resistance. Thermal Barrier Coating (TBC) is widely applied in gas turbine. This system consists of a bond coat, a Thermally Grown Oxide (TGO), and a ceramic top coat. Bond coat with formula of MCrAlY (M: Ni, Co, Fe, or both of these three, Y: reactive element) provides a good protection against high temperature oxidation [2, 3]. Many studies have stated that oxidation resistance occurs due to the TGO conditions. A continuous, adherence, and slow-growing of TGO protects high temperature components against oxidation [4].

Naumenko et al. studied that the addition of reactive element (e.g. Y, Si, Hf, Zr and La) could increase the TGO adherence [4]. Each reactive element has a different effect on TGO performance. Yttrium promotes formation of oxide pegs at interface between oxide scale and the underlying coating, and prevents scale rumpling [5,6]. In addition, silicon can produce protective oxide scale by formation
of SiO$_2$. Protective scale of silicon dioxide has a good oxidation resistance as well as alumina in high temperature. Therefore, a lot of studies of silicon addition on bond coat has been conducted for Ni-based superalloy [7-9]. However, the comparison of oxidation resistance in high temperature between NiCrAl with Y and YSi has not yet explored.

In the present study, the effect of Y and YSi addition on NiCrAl bond coat under oxidation test in air at elevated temperature of 1000 °C for 100 hours was investigated. The microstructure of bond coat with and without yttrium and yttrium-silicon provided information on the effect of Y and YSi reactive elements addition on NiCrAl coating that deposited on Hastelloy C-276.

2. Experimental procedures

Hastelloy C-276 substrate with composition balNi-15Mo-14Cr-4Fe-3W-2.5Co was cut into dimensions of 15×15×1.6 mm. The substrate was polished with a silicon carbide sand paper of #100 until final finishing of #1200. NiCrAlX coating powder was prepared by mechanical milling for 36 hours. The milling process produced an agglomerated particle with an average particle size of 130 µm. Table 1 shows the composition of coating powder.

| Coating Powder | Composition (wt.%) |
|----------------|--------------------|
| NiCrAlSi       | Bal 24 7          |
| NiCrAlY        | Bal 24 7 0.4 -    |
| NiCrAlYSi      | Bal 24 7 0.4 0.4  |

NiCrAlX was deposited using High Velocity Oxy Fuel (HVOF) method. This technology exhibits good performance on high adhesivity, low porosity, and high density [9]. Table 2 shows the parameter used in HVOF thermal spraying method. Afterwards, the coated samples were exposed to heat treatment in a vacuum (20 Pa) at 1100 °C for 4 hours in order to increase the adhesion of coating to the substrate. Isothermal oxidation was carried out at 1000 °C for 100 hours in air condition.

The heat-treated and oxidized samples were analyzed by X-Ray diffractometer (Rigaku Smart Lab Type) to identify phases. Surface morphology and micro-structural characterizations were carried out using a Field Emission Scanning Electron Microscope (FE-SEM) equipped with Energy Dispersive Spectroscopy (EDS) (JEOL JIB4610F).

3. Results and discussion

3.1. Isothermal oxidation

Figure 1 shows the mass change of NiCrAlX coating. The mass change was grouped into 3 stages as shown in table 3. The result shows that increasing in mass gain at initial stage of oxidation is due to the rapid formation of meta-stable oxide on the coating surface. Mass steady indicated low formation of oxides and less diffusion of oxygen to form oxides. Result in table 3 reveals that the mass steady of NiCrAlY specimen was lower than NiCrAl and NiCrAlYSi samples. According to figure 1, the scale spallation only appeared on NiCrAl of oxidized sample after 31 hours exposure and it indicated the failure protective scheme. It is also verified by the appearance of photograph sample which indicated the scale spalling occurred only on NiCrAl specimen as shown in figure 2. It is concluded that NiCrAlY sample had the best oxidation resistance due to the lowest mass change after 100 hours of oxidation exposure.
### Table 3. Three stages of mass change.

| Stage   | Mass Change (mg/cm²) |
|---------|----------------------|
| NiCrAl  | 3.2019               |
| NiCrAlY | 2.0247               |
| NiCrAlYSi | 3.1556             |

|               | mass gain | mass steady/loss | total   |
|---------------|-----------|------------------|---------|
| NiCrAl        | 3.2019    | -2.86            | 0.342   |
| NiCrAlY       | 2.0247    | 0.369            | 2.394   |
| NiCrAlYSi     | 3.1556    | 0.493            | 3.649   |

**Figure 1.** Mass change after isothermal oxidation in 1000 °C of three types coated sample (a) NiCrAl, (b) NiCrAlY, and (c) NiCrAlYSi.

**Figure 2.** Visual images of coated sample before and after oxidation: (a) NiCrAl, (b) NiCrAlY, and (c) NiCrAlYSi.

### 3.2. Surface morphology of oxide scale

Figure 3 shows the surface morphology of three types of coated samples before and after oxidation. It revealed that surface samples without reactive elements contained unmelted particles, whereas the samples with the addition of reactive element did not contain unmelted particles (figure 3 top). The surface morphology changes gradually during oxidation process due to the interaction with oxygen. Consequently, a typical cauliflower-like structure with varying sizes were observed on the surface of all oxidized samples [10].

**Figure 3.** SEI images of surface morphology of coated sample before (top) and after oxidation (bottom): (a) NiCrAl, (b) NiCrAlY, and (c) NiCrAlYSi.
3.3. Microstructure of oxide scale

Figure 4 shows the cross sectional structure of coated sample before and after oxidation. Coating thicknesses are measured above 200 μm. The sample consists of two layers which is secondary reaction zone (SRZ) and NiCrAl+/RE coating layer. Precipitates are formed in SRZ layer between substrate and coating layer due to the low solubility of Mo and Cr elements from Hastelloy substrate [10,11]. These precipitates improve the creep resistance of the substrate due to their grain boundary pinning action [1]. However, excessive quantities of SRZ formation decreases the mechanical properties of the substrate, thus it leads to unwanted phase formation [10,11]. The precipitate zones in NiCrAl decompose an amount of chromium and will cause spalling on the bond coat. On the contrary, in NiCrAlYSi sample, the secondary reaction zone is lower than the other two samples of NiCrAl and NiCrAlY due to the existence of silicon. Silicon as a reactive element could prevent outward diffusion of refractory elements of Mo from the substrate [7]. Therefore, a refractory precipitate was just observed in NiCrAl and NiCrAlY, which was indicated by bright gray area in the vicinity of coating interface.

Furthermore, a refractory precipitate is remained in NiCrAl sample after oxidation. It might aggravates internal stress at the coating/substrate interface which could result in mechanical failure of the coating system [3]. This result corresponds to the mass loss as shown in figure 1 for NiCrAl sample. However, the spalling area is not occurred on entire of oxidized sample. Therefore, the coating and oxide layer could observe as shown in figure 4a. Spallation of coating layer was also due to the excessive intensity of the oxide interface in the NiCrAl sample, which worsens the internal stress and causes TB failure [3]. In the case of NiCrAlY and NiCrAlYSi samples, oxide is observed not only on the top surface but also in coating layer indicated as black area in figure 4.

Figure 4. BSE images of cross sectional structure of coated sample before (top) and after oxidation (bottom): (a) NiCrAl, (b) NiCrAlY and (c) NiCrAlYSi.

Figure 5 shows cross sectional structure of oxide scale on the top layer (TGO) after 100 hours oxidation. The thickness of the oxide scale is about 1.03 μm, 1.18 μm, 1.17 μm on the top layer of NiCrAl, NiCrAlY, and NiCrAlYSi, respectively. According to the elemental mapping, the oxide scale consists of Cr, Ni, Al, and O constituents. This oxide scale is formed with duplex scale of spinel structure in the outer scale and stable alumina in the inner scale as indicated by arrow marked in figure 5. The detrimental mixed oxides are found to be preferred sites of crack nucleation, leading to premature TBC failure on the bond coat for a long time oxidation exposure [13]. Rumpling,
continuous, and thin TGO layer are found in NiCrAl sample as shown in figure 5a. The rumpling of TGO can initiate the failure of coating system [6] thus it is also confirmed that NiCrAl sample has less oxidation resistance. Moreover, thick and continuous TGO layer is observed in NiCrAlY sample. Mixed oxide is randomly distributed on the outer scale. Elemental mapping analysis also indicates that high intensity of aluminium and oxygen covered the NiCrAlY sample figure 5b bottom . It is assumed that stabilized alumina was formed in TGO layer. In contrast, a quite thick mixed oxide and discontinuous TGO layer is observed in NiCrAlYSi sample. Silicon addition in this coating sample could hardly prevent the formation of thick mixed oxide.

Figure 5. Enlargement images on top layer of coated sample after 100 hours oxidation: (a) NiCrAl, (b) NiCrAlY, and (c) NiCrAlYSi.

3.4. Phase formation
Figure 6 shows the XRD patterns before and after oxidation of NiCrAl (green), NiCrAlY (red), and NiCrAlYSi (blue) coated samples. The results showed that $\gamma$-Ni and $\gamma'$-Ni$_3$Al with cubic structure formed in all coated samples. The phase of $\gamma$-Ni increase mechanical properties [14] whereas $\gamma'$-Ni$_3$Al contributes to promote the Al$_2$O$_3$ formation during heating period [11]. On the heat treated sample, a hexagonal structure of Cr$_2$O$_3$ only observed in the sample without reactive element. The stable alumina ($\alpha$-Al$_2$O$_3$) with rhombohedral structure was formed on NiCrAlY and NiCrAlYSi sample while NiCrAlYSi and NiCrAl sample identified meta-stable alumina $\theta$-Al$_2$O$_3$ (monoclinic structure).

NiCr$_2$O$_4$ as a spinel oxide was formed in all oxidized samples and it confirmed the existence of mixed oxide with spinel structure in the outer scale of figure 5. The expected phase on oxidized sample was protective oxide. However, on NiCrAl sample after oxidation could not be identified as protective oxide, unlike on the spallation part such as meta-stable and stable alumina. Protective oxide was formed on NiCrAlY and NiCrAlYSi sample after oxidation. The results confirmed that coating with reactive element has good oxidation protective than coating without reactive element.
4. Conclusions
NiCrAlX coating was successfully developed on Hastelloy C-276 substrate by HVOF thermal spraying method. The following conclusions can be drawn from the results:
(1) Yttrium addition has improved the oxidation resistance of NiCrAl coatings.
(2) Silicon addition could prevent outward diffusion of Mo from the substrate and it increased the adherence of bond coat interface. However, silicon hardly suppresses the formation of thick spinel oxide.
(3) TBC failure was indicated by spallation of coating layer in NiCrAl oxidized sample which consisting of meta-stable and stable alumina after 31 hours oxidation.
(4) Meta-stable \(\theta\)-Al\(_2\)O\(_3\) and stable \(\alpha\)-Al\(_2\)O\(_3\) were formed in NiCrAlY and NiCrAlYSi oxidized sample, however a continuous of stable \(\alpha\)-Al\(_2\)O\(_3\) was only formed in NiCrAlY coated sample.
(5) NiCrAlY had the best oxidation resistance with total mass change of \(\pm 2.394\ \text{mg/cm}^2\) after 100 hours of oxidation.

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