The effect of silicon as a reactive element for NiCrAl coating performance on hastelloy substrate

S Ramandhany1,2, E Sugiarti1, R D Desiati1, E Martides3, E Junianto3, B Prawara3 and A Sukarto1

1 Laboratory of High Temperature Materials and Coatings, Research Centre for Physics, Indonesian Institute of Sciences (LIPI), Serpong 15314, Indonesia
2 Physics Division, Faculty of Science and Technology, State Islamic University of Jakarta 15411, Indonesia
3 Research Centre for Electrical Power and Mechatronics, Indonesian Institute of Sciences (LIPI), Komplek LIPI, Sangkuriang St., Building 20, Bandung, West Java 40135, Indonesia

enis002@lipi.go.id

Abstract. The isothermal oxidation behavior, microstructure, phase formation and microhardness of NiCrAl coatings with and without silicon addition were investigated. Characterization of heat treated and oxidized samples were carried out by X-ray diffractometer (XRD), scanning electron microscope (SEM) and vicker hardness tester. The NiCrAl and NiCrAlSi coatings were deposited with high velocity oxygen fuel (HVOF) on the surface of hastelloy substrate. Oxide scales consists of Al2O3 and NiCr2O4 phases were formed on the surface of coating sample after isothermal oxidation at temperature of 1000 °C for 100 hours. The addition of silicon increases the oxidation resistance of NiCrAl coating through the formation of Al2O3 phase, whereas on NiCrAl coating without silicon addition, mass loss was observed, which indicated scale spallation. The addition of silicon at 0.4wt% can prevent outward diffusion of refractory elements such as Mo from the hastelloy substrate. The measured hardness of NiCrAl and NiCrAlSi coatings were 317.53 and 330.9 Hv, respectively. The experimental results showed that NiCrAl with silicon addition improved the resistance of high temperature oxidation and hardness.

1. Introduction

Materials used for turbine blades should be able to be operated on extreme condition, where high temperature and mechanical properties is required [1]. Nickel-based alloy such as hastealloy or inconel offers the mechanical properties required to be used as turbine blades [1]. However, these superalloy metals properties are not sufficient enough to be operated on high temperature [2]. Therefore, coatings, such as thermal barrier coating (TBC), have been applied to the alloy to improve its performance at higher temperature [3]. A bond coat as part of TBC layer must be introduced as an interface to the metals and the coating. The MCrAlY (M: Ni, Fe, Co or combination of them) materials are widely used as a bond coat in many complicated and aggressive service environments [4].

In the MCrAl systems, addition of reactive elements such as silicon is well known to improve the oxidation resistance [2, 5]. Silicon has ability to increase oxidation resistance comes due to its ability...
to prevent refractory diffusion, such as tungsten or molybdenum [2]. Moreover, silicon addition to the alloy has been proven to increase its hardness, thus increasing its mechanical properties [6]. Similar studies of the addition of silicon as reactive elements have been investigated by J. Ma, et al. (2012) and J. Cao, et al. (2017) [4,7]. However, both studies have not presented microhardness test result to determine the mechanical properties of coating. Therefore, further investigation on the effect of silicon addition to the MCrAl bond coat system is still important.

Present study will explore the effect of silicon addition as reactive element to the performance of material coatings. Oxidation test at 1000 °C for 100 hours and hardness test will be carried out to investigate the oxidation resistance of coatings and the material strength, respectively. Coatings morphology and phase formation will also be investigated to obtain information regarding the effect of silicon addition.

2. Experimental procedures
Hastealloy C-276 with 1.6 mm thickness was prepared as substrate with a size of 15x15 mm². Prior to coating, the substrate was polished with silicon carbide sand paper #100 up to #800. NiCrAl coating was deposited into the substrate using HVOF spraying technique. The parameters of HVOF coating is summarized in Table 1 and the composition of coating was specified in Table 2. Coating powder was milled beforehand with a planetary ball mill (SFM-1 Desktop type) for 36 hours with a rotation speed of 1500 rpm.

Table 1. Composition of coating powder.

| N₂ pressure   | 4.8 bar |
|---------------|---------|
| O₂ pressure   | 8.2 bar |
| Propane pressure | 5.2 bar |
| Air screw compressor | 4 bar   |
| Fuel gas     | 60 lt/min |

Table 2. The composition of HVOF coating.

| Powder      | Composition (wt%) |
|-------------|-------------------|
| NiCrAl      | Bal 24 7 -        |
| NiCrAlSi    | Bal 24 7 0.4      |

Samples were grit blasted with silica powder in order to improve adhesion between coating and substrate. After coating process, sample was sintered at 1100 °C for 4 hours under vacuum condition to ensure the uniformity of coating and formation of expected phases. Oxidation test was carried out on the sample after heat treatment with isothermal oxidation method at temperature of 1000 °C for 100 hours.

The samples were characterized with X-ray diffraction (Smart Lab, Rigaku) with Cu-Kα wavelength and scanning electron microscope (JIB2010F, JEOL) equipped with energy dispersive spectroscopy. The influence of silicon addition on hardness was investigated through micro-vickers hardness tested (LM100AT, LECO) under 300 gf load and dwell time of 13 seconds.

3. Results and discussion

3.1 Isothermal oxidation
Figure 1 shows the mass change of NiCrAl and NiCrAlSi coated samples after isothermal oxidation process. Both samples show a rapid increase in mass during the early stage of oxidation test due to the formation of oxides on samples [8]. To investigate the mass change rate, the graph was sectioned into two parts and mass change rate are calculated from the equation:

\[(\Delta m/A)^2 = k_p T\]  \hspace{1cm} (1)

During the early part, from 0 hours until 31 hours of oxidation test, both samples have a positive mass change rate, which means that the formation of oxide scales still occur until 31 hours of
oxidation. Samples coated without silicon additives are found to have higher mass change rate than the samples that are coated with silicon additives.

On the later part of oxidation test, from 31 until 100 hours of oxidation, mass change process started to differentiate between both samples. Samples coated without silicon addition was found to have a significant mass loss with a rate of $-3.29 \times 10^{-11}$ mg$^2$cm$^{-4}$s$^{-2}$, which means that a breakdown condition occurs on the coating. This breakdown was indicated through scale spallation. On the other hand, samples coated with silicon addition did not have a breakdown phenomenon. The NiCrAlSi coated sample have a steady mass increase from 31 hours with a rate of $3.83 \times 10^{-13}$ mg$^2$cm$^{-4}$s$^{-2}$, which means that the sample successfully form a protective layer and prevent the coating from breakdown phenomenon.

### Table 3. Parabolic constant of curve mass change.

| Stage       | $Kp$ (mg$^2$cm$^{-4}$s$^{-2}$) | NiCrAl | NiCrAlSi |
|-------------|--------------------------------|-------|----------|
| 0h-31h      | 9.19 x 10$^{-11}$              | 4.93 x 10$^{-11}$ |
| 31h-100h    | -3.29 x 10$^{-11}$             | 3.83 x 10$^{-13}$ |

**Figure 1.** Mass change after isothermal oxidation in 1000 °C of types coated sample (a) NiCrAl, (b) NiCrAlSi.

3.2 Microstructure morphology

Morphology of coated samples are able to be observed from Figure 2. It can be identified that the samples are composed of an oxide layer, coating layer and secondary reaction zone (SRZ). The oxide layers were formed when the NiCrAl powder reacts with oxygen to form oxide phases, such as $\text{Cr}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$. Most of this oxide layer are formed on the top part of coating which are exposed to the air. Inset of each sample coating images show that most oxide is located on top of the coating. These oxide layers plays an important part to increase sample oxidation resistance [5, 11].

Both NiCrAl and NiCrAlSi coating layer are easily identified from the cross-section images, this part of coating is the thickest and composed of $\gamma'$-Ni$_3$Al and alumina ($\text{Al}_2\text{O}_3$) phases. Alumina phases were formed when oxygen able to diffuse through the porous coating and reacts with aluminium, thus preventing the oxygen from moving further into the substrate. Therefore, a formation of alumina phases indicated that oxygen diffusion is limited [11].

Precipitates of molybdenum of element which are formed below the coating layer are able to be identified as the secondary reaction zone (SRZ). The SRZ would improve the material creep resistance; however, large amount of SRZ will instead decrease mechanical properties of the coating. The spallation on NiCrAl coated sample while oxidation test was caused by the excessive amount of SRZ.

3.3 Phase identification

Figure 3 shows the XRD characterization result for NiCrAl (a, a.1) and NiCrAlSi (b, b.1) coated sample, before and after oxidation. In addition, spallation NiCrAl coating was also characterized with XRD (a.3). From the characterization result, it can be observed that NiCrAl coating produce different peaks compared to the NiCrAlSi coating. On the NiCrAl coated sample chromium oxide are detected,
while on NiCrAlSi coated sample no chromium oxide was present. This could happen due to the addition of silicon as reactive elements. The presence of silicon as additives cause the oxygen to diffuse less and reacts with $\gamma'$-Ni$_3$Al to form protective layer of alumina according to equation (2).

$$2 \gamma'-\text{Ni}_3\text{Al} + 3[O] \rightarrow \text{Al}_2\text{O}_3 + 6\text{Ni} \tag{2}$$

Without the presence of silicon oxygen diffuses freely and reacts with alumina to form $\theta$-alumina and chromium to form chromium oxide according to equation (3).

$$2[\text{Cr}] + 3[O] \rightarrow \text{Cr}_2\text{O}_3 \tag{3}$$

After the oxidation test it is found that metastable $\theta$-alumina change phases into $\alpha$-alumina which are more stable. NiCrAl coated sample have a less amounts of $\alpha$-alumina phases after the oxidation test, however $\alpha$-alumina phases of NiCrAl coating are found to be located on the spallation. This led to the conclusion that large SRZ have lesser adhesion with alumina, and caused the coating to spall. In addition, the presence of chromium oxide led to the formation of spinel structure that is detrimental to the coating performance. The formation of spinel is presented in equation (4).

$$\text{NiO} + \text{Cr}_2\text{O}_3 \rightarrow \text{NiCr}_2\text{O}_4 \tag{4}$$

![Figure 2](image-url).Cross section microstructure of (a) NiCrAl and (b) NiCrAlSi coated sample before oxidation test. Cross section microstructure of (a.2) NiCrAl and (b.2) NiCrAlSi after oxidation test.

### 3.4 Microhardness

Figure 4 and Table 4 show the result of microhardness characterisation using the micro-vickers hardness tester. Hardness value of NiCrAl and NiCrAlSi coated sample are found to be similar before the oxidation test. However, after the oxidation test the hardness value of substrate and coating changes differently. NiCrAlSi coating shows an increase in hardness value due to the formation of oxide protective layers, while on NiCrAl coating a decrease in hardness value was observed due to the spallation.

The coated substrates show an increase in hardness value due to the oxidation test. After the oxidation test, SRZ can be observed to shrink and an interface oxide layer are formed on the substrate. The interface may form whenever oxygen diffuse through the porous coating and reacts with the
substrate. Higher hardness value in NiCrAl coated sample means that it has less protective ability that cause more oxygen to react with the substrate.

Figure 3. XRD pattern of the coated sample: (a.1) before and (a.2) after oxidation of NiCrAl coated sample with (a.3) spallation of NiCrAl, (b.1) before and (b.2) after oxidation of NiCrAlSi.

Figure 4. Vickers indents on (a)NiCrAl and (b) NiCrAlSi coated sample before oxidation. Vicker indents on (a.2) NiCrAl and (b.2) NiCrAlSi coated sample after oxidation test.

Table 4. Vickers microhardness at substrate and coating layer samples.

| Samples   | Before Oxidation (HV) | After Oxidation (HV) |
|-----------|-----------------------|----------------------|
|           | Substrate Coating     | Substrate Coating    |
| NiCrAl    | 182.84 355.43         | 243.43 317.53        |
| NiCrAlSi  | 185.44 288.3          | 205.84 330.9         |
4. Conclusions
The characterization of isothermal oxidation NiCrAl and NiCrAlSi coating on hastelloy substrate has been investigated. The conclusions of the investigation can be drawn as follows: (i) The presence of silicon as reactive element prevents breakdown condition of isothermal oxidation testing; (ii) Silicon addition to the NiCrAl coating are found to increase its hardness and promote the formation of $\alpha$-$\text{Al}_2\text{O}_3$ as protective oxides; (iii) NiCrAlSi coated sample able to withstand 100 oxidation test with mass gain rate of 2.56 mg/cm$^2$.

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