Structural and crystal orientation analysis of Al-Si coating on Ni-based superalloy by means of EBSD technique

To cite this article: A N Muslimin et al 2018 J. Phys.: Conf. Ser. 985 012020

View the article online for updates and enhancements.
Structural and crystal orientation analysis of Al-Si coating on Ni-based superalloy by means of EBSD technique

A N Muslimin¹, E Sugiarti¹³, T Artonang², R. I Purawiardi¹ and R D Desiati³

¹Laboratory of Focused Ion Beam, Research Centre for Physics, Indonesian Institute of Sciences (LIPI), Serpong 15314, Indonesia
²Department of Metallurgical Engineering, Faculty of Engineering, University of Sultan Ageng Tirtayasa, Cilogen 42124, Indonesia
³Laboratory of High Temperature Materials and Coatings, Research Centre for Physics, Indonesian Institute of Sciences (LIPI), Serpong 15314, Indonesia

E-mail: enis002@lipi.go.id

Abstract. Ni-based superalloy is widely used for high performance components in power generation turbine due to its excellent mechanical properties. However, Ni-based superalloy has low oxidation resistance. Therefore, surface coating is required to improve oxidation resistance at high temperatures. Al-Si as a coating material was successfully deposited on Ni-based substrate by pack cementation method at 900 °C for about 4 hours. The oxidation test was carried out at high temperature of 1000 °C for 100 hours. Micro structural characterization and analysis on crystal orientation were performed by using Field Emission Scanning Electron Microscope (FE-SEM) and Electron Back Scatter Diffraction (EBSD) technique, respectively. The results showed that the coating layer with a homogenous layer and had a thickness of about 53 μm consisting of β-NiAl with cubic structure and Ni₂Al₃ with hexagonal structure. TGO layer was developed after oxidation and had a thickness of about 5 μm consisting of α-Al₂O₃ and spinel NiCr₂O₄. The phase composition map and crystal orientation acquired by EBSD technique was also discussed both in TGO and coating layers.

1. Introduction

Ni-based superalloy is used in gas turbine engine component that require high creep resistance and fatigue strength at high operating temperatures. The applications of Ni-based superalloy in aggressive environment are subjected to oxidation and hot corrosion attacks. Surface coating has been one of solution to solve these problems for superalloys in harsh environment [1]. Aluminium (Al) is the most commonly used element for coating material due to the ability to form highly stable protective layer of Al₂O₃ in high temperature [2-4]. However, simple aluminate coating was not sufficient to withstand against high temperature oxidation and hot corrosion. Therefore, a combination of aluminate coating with silicon (Si) element was used to increase oxidation and hot corrosion resistance at high temperatures [5-11]. It has been known that Al-Si coating applied by a pack cementation method would formed β-NiAl and δ-Ni₂Al₃ phases in coating layer [12-13]. A thermally grown oxide (TGO) layer is formed at the surface of coating layer during high temperature oxidation. The TGO was mainly composed of mixed oxide containing α-Al₂O₃ and spinels Ni(Cr,Al)₂O₄ [1].

Recently, many researchers have studied the phase distribution and correlation towards microstructure of coating and TGO layer by FE-SEM and EBSD techniques [1, 14]. Wollmer et al.
investigated the micro structural and crystal orientations of β-NiAl and γ-Ni₃Al formed in the NiAl coating on superalloy substrate. In addition, Chmiela et al [1] studied microstructural and crystal orientation of thermal barrier coating with addition of Gd₂Zr₂O₇ as reactive element. It showed that EBSD is one of powerfull technique that can provide detailed information about the crystalline structure and crystallographic orientations of the grains. Therefore, the present research will investigate the microstructure, phase distribution, crystal structure, and crystal orientation of Al-Si coating as well as TGO layer before and after oxidation by using FE-SEM and EBSD technique.

2. Experimental

The Al-Si powder was coated on Ni-based superalloy by pack cementation method. The coating material has a composition of 2.6 wt.% Al, 10 wt.% Si, 4 wt.% NH₄Cl and 83.4 wt.% Al₂O₃. The pack cementation process was carried out at temperature of 900 °C for approximately 4 hours. The Al-Si coating samples were subjected to oxidation test at 1000 °C for 100 hours. A microstructural characterization was performed on cross sectional of Al-Si coating sample before and after oxidation by FE-SEM (JEOL JFIB-4610F) equipped with Energy Dispersive X-ray Spectroscopy (EDS, Oxford X-Max 50 detector). Crystal structure, crystal orientation and phase composition were evaluated by EBSD technique (Oxford Nordlys Max³ detector). Prior to EBSD analysis, the sample was cut in cross section with a size of 3×5×0.5 mm followed by mechanical polishing by SiC paper with a grid size from #100 to #3000 and final polished using Al₂O₃ suspension with a grid size 0.10 μm and 0.05 μm. A quantitative analysis was acquired by EDS technique with primary electron beam 15 kV and probe current number 13. Moreover, EBSD analysis was collected with condition of 20 kV electron beam and 14 probe current in order to optimize the data acquisition.

3. Results and discussions

3.1 Microstructure of Al-Si coating layer

Figure 1 shows cross sectional morphologies of Al-Si coating layer before and after oxidation. The result showed that the coating comprised of two layers: interdiffusion layer and Al-Si coating layer. Complex structure with irregular shape and different contrast in the interdiffusion zone (figure 1a) might indicated the inward and outward diffusion of nickel from the substrate and aluminium-silikon from the coating element.

A homogeneous layer with the thickness of 35 μm was formed on the Al-Si coating layer as shown in figure 1b. A TGO layer was entirely formed on the top surface of Al-Si coating layer as shown in figure 1c. A lot of voids were formed at the interface between Al-Si coating and TGO layers as clearly shown in SEI image of figure 1(c). The thickness of TGO layer was approximate 5 μm.

3.2 Quantitative analysis of Al-Si coating layer

EDS analysis were performed on the cross sectional of Al-Si coating layer before and after oxidation as shown in figures 2 and figure 3, respectively. According to the previous result, β-NiAl and δ-Ni₃Al phases have been identified in the Al-Si coating layer on Ni-based superalloy [12-13]. The results obtained in figure 2 revealed that Al-Si coating layer contained high intensity of nickel and aluminium (figures 2b - 2d). The compositions of each elements was notified in about 45 at.% Ni and 55 at.% Al. It is known that Ni with composition range of 45-60 at.% formed at temperature of 900 °C could identified as cubic structure of β-NiAl phase based on the binary phase diagram of Ni-Al system [15]. Therefore, the present results might indicated the formation of homogenous and stable β-NiAl in the whole part of Al-Si coating layer as shown in figure 2a. It is noticed that the composition of initial coating powder and temperature of pack cementation used in the present study would promote the formation of silicon-modified NiAl through inward diffusion of Al and Si as well as the outward diffusion of Ni. These results have a good agreement with the statement that Al is main element diffusion in NiAl phase when the content of Al in this phase is more than 41 at.% [15].
Figure 1. FE-SEM cross-section morphology of Al-Si coating layer: (a) and (b) BSE images of Al-Si coating sample before oxidation with magnification of 1000x and 1500x, respectively. (c) and (d) SEI and BSE images of Al-Si coating sample after oxidation.

Figure 2. Three points of EDS spectra obtained from Al-Si coating layer before oxidation.
Figure 3 shows the EDS analysis of Al-Si coating layer after oxidation. The peak intensity in point (1) showed high signal for aluminium and oxygen content which indicated by dark area as shown in figure 3a. In contrast, high intensity of nickel, aluminium, and small amount of chromium and silicon were obtained in the grey area of coating layer as shown in figure 3a. The high composition of nickel in the gray area might indicated the existance of stable β-NiAl phase and the formation of spinel NiCr$_2$O$_4$[1]. The results revealed that the outer layer was comprised of α-Al$_2$O$_3$ protective oxide. By the formation of a dense and continuous layer, a protective oxide could play an important part as diffusion barrier of oxygen to diffuse inward into the coating layer and substrate. The reason is because alpha alumina (α-Al$_2$O$_3$) is very stable because of its crystalline structure, thus it can reduce the diffusion rate of anions and cations [8].

![Figure 3](image)

Figure 3. Three points of EDS spectra obtained from Al-Si coating layer after oxidation.

3.3 Phase composition and crystal orientation of Al-Si coating layer before and after oxidation

EBSD analysis was initially obtained by acquiring the kikuchi pattern of selected area and by using a software, the kikuchi pattern is then considered indexed when its orientation and phases are known. Therefore, it is very important to store the candidate phases (table 1) prior to EBSD analysis. 

Figure 4 shows the phase composition map and crystal orientation of Al-Si coating layer before oxidation. The result revealed the major phase was β-NiAl which distributed 99.85 % in the selected area (20x20 μm) of Al-Si coating layer as indicated by blue region in figure 4a. The minor phases of Ni$_2$Al$_3$ was notified by 0.15% and indicated by dot marked in red color (figure 4a). Further, inverse pole figure (IPF) in z axis as shown in figure 4b revealed the crystal orientation correspond to its grain. A large grain with red color showed the crystal orientation of β-NiAl in <0 0 1> direction. Whereas, inside the β-NiAl grain, a very small grain of Ni$_2$Al$_3$ co-existed with the direction between <1 0 0 1> and <0 1 -1 0> as indicated by yellow color in figure 4b. A homogeneous β-NiAl with big grain showed that this phase was very stable and uniformly observed in the Al-Si coating layer. This result indicated that the existance of β-NiAl with cubic structure would increase the oxidation resistantance and the life time of the sample for the application [5].
Table 1. Crystal structure of identified phases.

| Phase name   | Crystallographic system | Space group | Unit cell parameter (nm) |
|--------------|--------------------------|-------------|--------------------------|
|              |                          |             | a₀ | b₀ | c₀ |
| β-NiAl       | Cubic                    | Pm-3m       | 2.88 | 2.88 | 2.88 |
| Ni₃Al₃       | Hexagonal                | P-3m1       | 4.065 | 4.065 | 4.906 |
| α-Al₂O₃      | Rhombohedral             | R-3c        | 4.759 | 4.759 | 12.99 |
| NiCr₂O₄      | Tetragonal               | I 41/amd    | 5.760 | 5.760 | 8.50  |

Figure 4. EBSD investigation of Al-Si coating sample before oxidation: (a) phase composition map and (b) IPF Z crystal orientation.

Figure 5. EBSD investigation of Al-Si coating sample after oxidation: (a) and (c) phase composition map of TGO and coating layer, respectively. (b) and (d) IPF Z crystal orientation of TGO and coating layer, respectively.

EBSD analysis in Al-Si coating after oxidation is shown in figure 5. EBSD analysis was captured in TGO and coating layer with observing area of 15×15 µm. It has been understood from SEM result
that the thickness of TGO was about 5 μm. Therefore, EBSD analysis in TGO layer was captured in the interface between TGO and coating layer as shown in figures 5a and 5b. The results showed that NiAl, Cr$_2$NiO$_4$ and Al$_2$O$_3$ had a percentage of 16.25%, 15.57% and 4.73% in the observing area, respectively. Al$_2$O$_3$ with red region in figure 5a had a smaller grain structure than NiAl and Cr$_2$NiO$_4$. Moreover, Cr$_2$NiO$_4$ coexisted in NiAl grain structure which indicated by yellow and blue region in figure 5a. Black region in phase composition map and inverse pole figure (IPF) image indicated non-indexed area. By IPF in z axis, it showed that the crystal orientation of Al$_2$O$_3$ was on $<0\ 0\ 0\ 1>$ plane direction, β-NiAl was on $<1\ 1\ 1>$ plane direction, and NiCr$_2$O$_4$ was on $<0\ 0\ 1>$ plane direction in TGO layer. Moreover, the crystal orientation of β-NiAl was between $<1\ 1\ 1>$ and $<0\ 0\ 1>$ plane direction and NiCr$_2$O$_4$ was between $<0\ 0\ 1>$ and $<1\ 1\ 1>$ plane direction.

4. Conclusion

Microstructure, phase composition, and crystal orientation of Al-Si coating samples were successfully investigated by using FE-SEM and EBSD techniques. Al-Si coating layer developed by pack cementation process at temperature of 900 °C had a homogeneous layer with the thickness of 35 μm. The quantitative of EDS analysis showed that the composition of Ni-Al in the coating layer indicated the existence of β-NiAl with cubic structure having 99.85% of phase map from EBSD analysis. β-NiAl had a large grain with crystal orientation of $<0\ 0\ 1>$ direction in the Al-Si coating layer before oxidation. Ni$_2$Al$_3$ had also been identified in the coating layer before oxidation with the phase composition of 0.15%. After oxidation, TGO layer was growth on the top surface of Al-Si coating layer with a thickness of about 5 μm which comprised of protective oxide of Al$_2$O$_3$ and spinel oxide of NiCr$_2$O$_4$. Crystal orientation of Al$_2$O$_3$ was on $<0\ 0\ 0\ 1>$ plane direction and NiCr$_2$O$_4$ was on $<0\ 0\ 1>$ plane direction in TGO layer. Spinel oxide of NiCr$_2$O$_4$ was formed both in TGO and coating layers after oxidation. This phase is formed from reaction between Cr$_2$O$_3$ and NiO before the continuous oxida scale of Cr$_2$O$_3$ formed. Spinel Cr$_2$NiO$_4$ can act as a diffusion barrier of Ni ions thus preventing the formation of excessive unprotected Ni oxide. In addition, a protective oxide of Al$_2$O$_3$ formed in TGO layer could improved the oxidation resistance of Ni-based superalloy for high temperature applications.

Acknowledgments

The authors would like to thank to Kegiatan Unggulan LIPI, INSINAS IRPI grant No. 04/INS-2/PPK/E/E4/2017 and 2016 Toray Science Technology Research Grant for financial support of this work.

References

[1] Chmiela B, Sozanska M and Moskal G 2012 IOP: Conf. Ser.: Mater. Sci. Eng. 32 012006
[2] Xiang Z D, Datta P K 2003 Mater. Sci. Technol. 19 935
[3] Multinitalapati N R 2011 Advances in Gas Turbine Technology 22905
[4] Tong L, Dengzun Y and Chungen Z 2010 Chinese. J. Aeronaut. 23 381
[5] Tu X, Peng H, Zheng L, Qi W, He J, Guo H and Gong S 2015 Appl. Surf. Sci. 325 20
[6] Fu C, Kang W K and Cao G H 2014 Surf. Coat. Technol. 258 347
[7] Wang K L, Chen F S and Leu G S 2003 Mater. Sci. Eng. A 357 27
[8] Fan Q X, Jiang S M and Wu D L, Gong J 2013 Corros. Sci. 76 373
[9] Liu C T, Ma J, Sun X F and Zhao P C 2010 Surf. Coat. Technol. 204 3641
[10] Xiang Z D, Burnell-Gray J S and Datta P K 2001 J. Mater. Sci. 36 5673
[11] Mansuri M, Hadavi S M M and Zare E 2016 Metall. Mater. Trans. A 47 293
[12] Bozza F, Bolelli G, Giolli C, Giorgetti A, Lusvarghi L, Sassatelli P, Scrivani A, Candel A and Thoma M 2014 Surf. Coat. Technol. 239 147
[13] Arabi H, Rastgari S, Salehpour Z and Bakhshi A 2008 Inter. J. Eng. Sci. 19 39
[14] Wöllmer S, Zaefferer S, Göken M, Mack T and Glatzel U 2003 Surf. Coat. Technol. 167 83
[15] Kitahara H, Ueki R, Ueda M, Tsuji N and Minamino Y 2005 Mater. Charact. 54 378