Coating of Nickel Aluminide by Pack Cementation to Improve Oxidation Resistance of Nickel-Based Superalloy, Grade IN 738

Patama Visuttipitukul[1], Sirinya Chansaksoong[2] and Panyawat Wangyao[1*],

[1]*Department of Metallurgical Engineering, Faculty of Engineering,*
[2]*Graduate School of Engineering, Faculty of Engineering,*
Chulalongkorn University, Bangkok, Thailand

(Received November 26,2009)

ABSTRACT

Nickel-based superalloys grade IN 738 were aluminized and annealed to improve oxidation resistance. The sample surface was analyzed by GIXD after aluminizing, annealing and oxidation testing. The microstructure of the coating layer was observed by optical microscope and SEM. EDS was employed to investigate distribution of elements in the coating layer. The thickness of the coating layer increased with increasing time and temperature. The growth rate of the nickel-aluminide layer increased from 0.95 to 1.55 and 3.47 $\mu m/s^{1/2}$ when the aluminizing temperature increased from 1073 to 1173 and 1273K. The aluminizing temperature played an important role in the structure of coating. When aluminizing at 1073 and 1173 K, a fine structure of Ni_2Al_3 formed as a coating layer by inward diffusion of aluminum. For 1273 K aluminizing, large columnar grains of Ni_2Al_3 coexisting with $AlCr_2$ were formed by both outward and inward diffusion. Annealing can homogenize the coating layer. Ni_2Al_3 can be changed to the NiAl phase by annealing at 1273 K for 36 ks under argon atmosphere. Oxidation resistance of IN738 was markedly increased by aluminizing and annealing because of the formation of aluminum-oxide film as a protective film.

Keywords: pack cementation, nickel aluminide, oxidation resistance, nickel-based superalloys

1. INTRODUCTION

The major degradations and failure usually found in cast nickel-based superalloy grade IN738 result from high-temperature oxidation and hot corrosion processes. To achieve high resistance of both processes, chromium can be added up to 15wt% to form Cr_2O_3 film combined with Al_2O_3 for a protective oxide scale film. However, addition of Cr by more than 20 wt% could lead to σ-phase formation resulting in brittle fracture of material. Therefore, surface modifications by coating are utilized to improve oxidation-resistant nickel-based superalloys /1-3/. Aluminizing by means of pack cementation is one of the surface modification processes which can provide a nickel-aluminide coating which acts as a protective layer in order to improve oxidation resistance. Among several nickel-aluminide compounds, NiAl is an intermetallic compound which has excellent oxidation resistance /4,5/. Formation of the NiAl coating layer on the substrate could resist oxidation and prolong the lifetime of the nickel-based superalloy. To achieve a thick NiAl layer with a fine coating structure,

---

*Corresponding author: Dr. Panyawat Wangyao.
Tel.: +662-218-6933; E-mail:panyawat@hotmail.com

the process parameters must be considered. Using high-temperature aluminizing can prevent formation of other nickel-aluminide compounds such as Al_3Ni_5 and Al_3Ni which are not stable at high temperatures. However, too high process temperatures can lead to crack formation due to different thermal-expansion coefficients of the matrix and coating layer. Also the formation of micro pores in the matrix due to the Kirkendall Effect (which decreases mechanical strength) must be avoided /6-8/. In this research, the formation of a nickel-aluminide layer by pack aluminizing at various times and temperatures was studied. The effect of annealing after aluminizing on a coating layer was also studied. The oxidation resistance of the cast and coated sample was investigated.

2. EXPERIMENTAL PROCEDURE

A nickel-based superalloy grade IN 738 was selected as a substrate to evaluate the optimum condition of pack cementation and oxidation resistance after coating. IN 738 was cut into a rectangular shape and polished by SiC paper followed by 1μm Al_2O_3 powder. After polishing, the samples were rinsed and cleaned by ultrasonic bath using acetone for 300 seconds.

In this study, pack cementation of IN 738 was divided into two steps: aluminizing and annealing. For the aluminizing step, the samples were placed in an alumina crucible with an aluminizing reagent. The aluminizing reagent was a mixture of aluminum powder, ammonium chloride and alumina powder with weight ratio of 15:5:80. The aluminizing processes were performed under argon atmosphere with temperature varying from 1023 to 1273 K (800 to 1000°C) for 3.6 to 22.5 ks (1 to 6.25 hours). After aluminizing, all samples were annealed at 1273 K for 21.6 to 36 ks (6 to 10 hours) under argon atmosphere in order to prevent oxidation. Oxidation testing was conducted by using a vertical tube furnace at 1273 K for 144 ks (40 hours) under ambient atmosphere.

The samples, after coating, annealing and oxidation testing, were characterized by energy dispersive spectrometer (EDS), and glancing incident angle x-ray diffraction (GIXD), at the incident angle of 5 degrees. The microstructure was observed by use of a scanning electron microscope (SEM), and an optical microscope.

3. RESULTS AND DISCUSSION

The coating layer thickness increased with increasing aluminizing time and temperature. Plots of the coating thickness against the square root of the aluminizing time are shown in **Fig. 1**. The incubation time can be neglected as can be seen from Fig. 1 whereby the intercept of the trend line is close to the point of origin. The small value for the incubation time implies that the ratio of the powdered mixture in the pack used in this study was appropriate for aluminizing nickel-based super alloys grade IN738. The linear relationship between thickness and the square root of the aluminizing time suggests that the diffusion process controlled growth of the coating layer. As shown in Fig. 1, the growth rates of the coating layer were 0.95, 1.55 and 3.47 $\mu m/s^{1/2}$ (42.74, 92.79 and 208.46 $\mu m/hour^{1/2}$, respectively) when aluminized at 1073, 1173 and 1273 K, respectively. The growth rate increased when the aluminizing temperature increased since the diffusion process was activated by the higher temperatures, resulting in a higher diffusion rate.

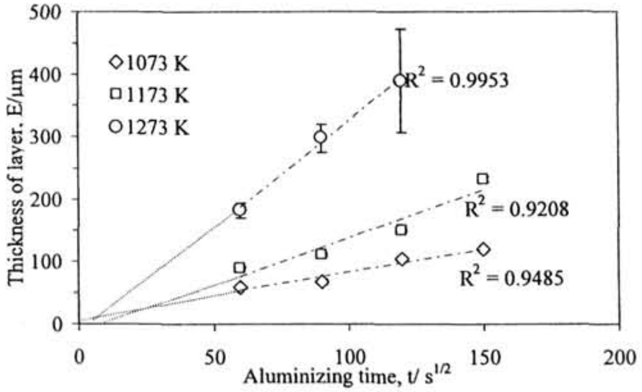

Fig. 1: Thickness of coating layer against aluminizing time.

For 1073 and 1173 K aluminizing temperatures, which are considered low temperatures for aluminizing in this research, the microstructure of the coating layer was a fine and uniform structure for all aluminizing times as shown in **Fig. 2**.

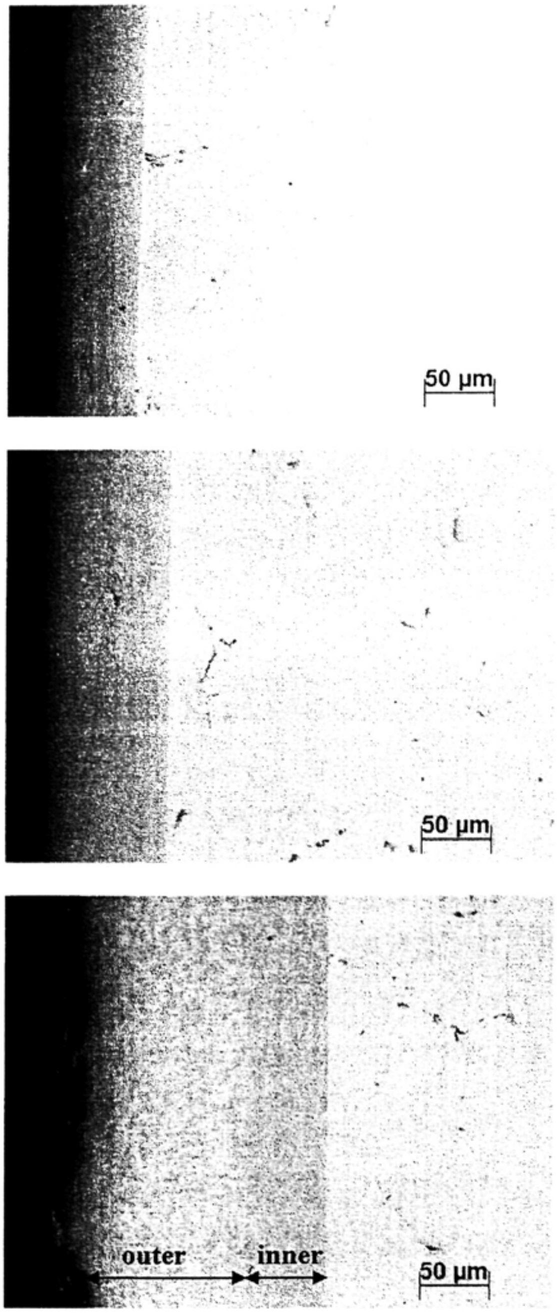

Fig. 2: Cross-section microstructure of aluminized IN738 for 3.6 ks at (a) 1073 K, (b) 1173 K and (c) 1273 K.

GIXD analysis at the surface of samples shows that the coating layers consisted of Ni_2Al_3 and $NiAl_3$ (see **Fig. 3**).

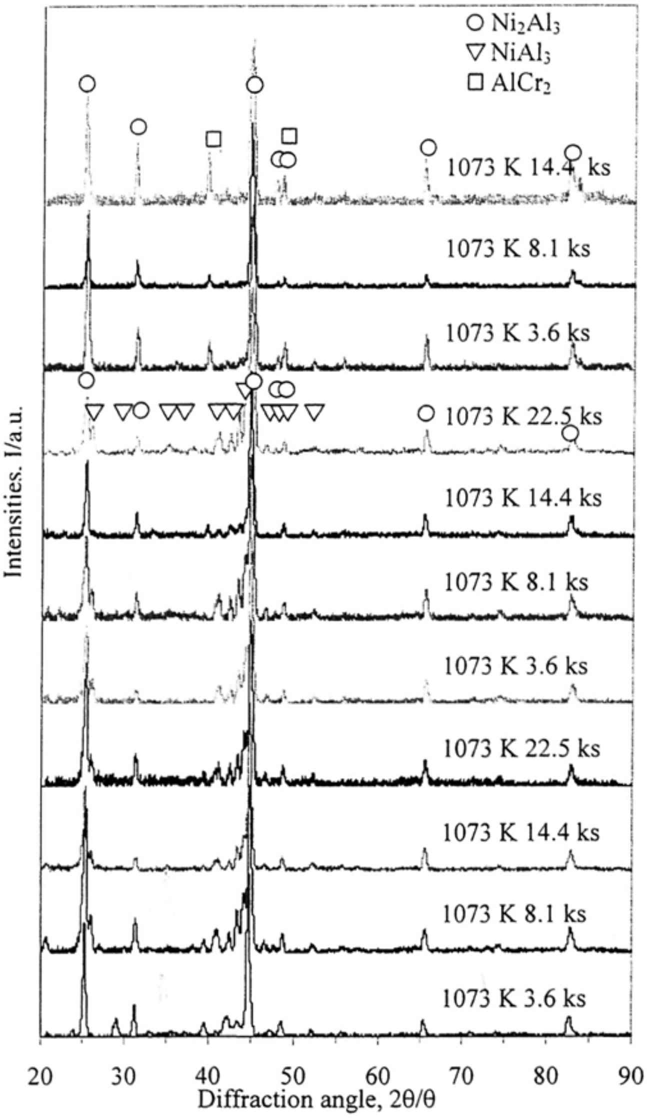

Fig. 3: GIXD profiles of IN738 after aluminizing.

The high relative intensities of the Ni_2Al_3 peaks indicate that Ni_2Al_3 was the main phase in the coating layer formed by 1073 and 1173 K aluminizing. When the aluminizing temperature was increased to 1273 K, which is considered a high temperature for aluminizing, a non-uniform microstructure of the coating layer was observed **(Fig. 2 (c))**. The layer coated at the high temperature for aluminizing of 1273 K can be divided into two zones: inner and outer. The inner zone, which is located adjacent to the matrix, had a fine structure similar to those structures of the layers formed by low-temperature aluminizing at 1073 and 1173 K. The outer layer had a rough structure consisting of two phases: dark grey and light grey. Both phases contained aluminum but the dark-grey phase was a chromium-rich phase while the light-grey phase was a nickel-rich phase as shown by elemental line scans in **Fig. 4**.

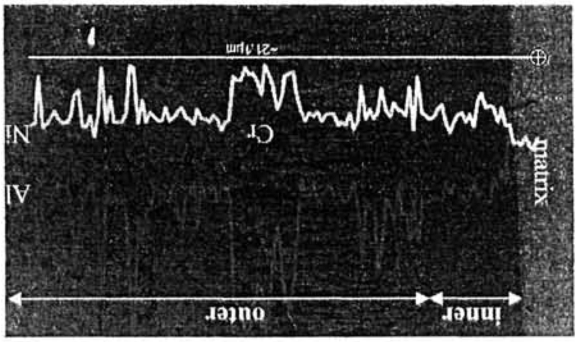

Fig. 4: Line scan of nickel (green line), chromium (red line) and aluminum (blue line).

Since the GIXD analysis shows that the coating layer consisted of Ni_2Al_3 and $AlCr_2$, the dark-grey phase can be identified as $AlCr_2$, and the light-grey phase was Ni_2Al_3. $NiAl_3$ was not found in this coating layer because the $NiAl_3$ is not stable at 1273K. The different main phase and microstructure in the coating layer shows that for low-temperature aluminizing (1073 and 1173 K), the growth of the aluminizing layer was controlled by inward diffusion of aluminum into IN738 resulting in a fine microstructure of Ni_2Al_3 phase. In contrast, for 1273K aluminizing, both inward and outward diffusion processes took place as can be seen from the two sub-layer coating layers in Fig. 2 (c). The inner sub-layer was formed by inward diffusion of aluminum while the outer sub-layer was formed by both inward and outward diffusion, resulting in a rough structure. The outer sub-layer consisted of columnar grains in a perpendicular direction to the sample surface which suggests that there was outward diffusion of nickel and chromium from the matrix. Outward diffusion normally occurs when the aluminizing temperature exceeds 1273K /3/. Although a high temperature can achieve a high growth rate of the coating layer, the outward diffusion of nickel from the matrix to the coating layer can cause formation of micro pores (the Kirkendall Effect). According to the previously described results, 1173 K (900°C) would be the most appropriate aluminizing temperature. At this coating temperature, the microstructure of the coating

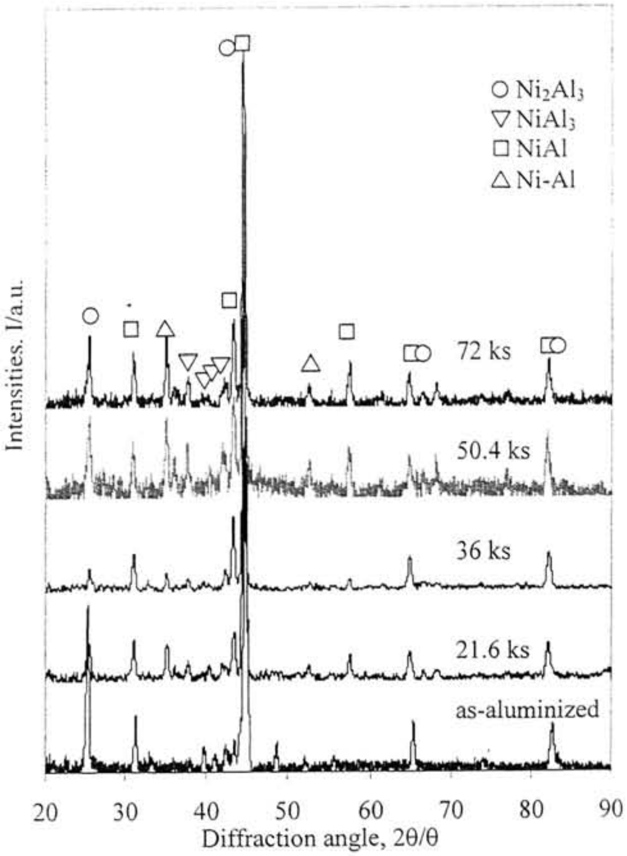

Fig. 5: GIXD profiles of IN738 after aluminizing at 1173 K for 14.4 ks following by various annealing time.

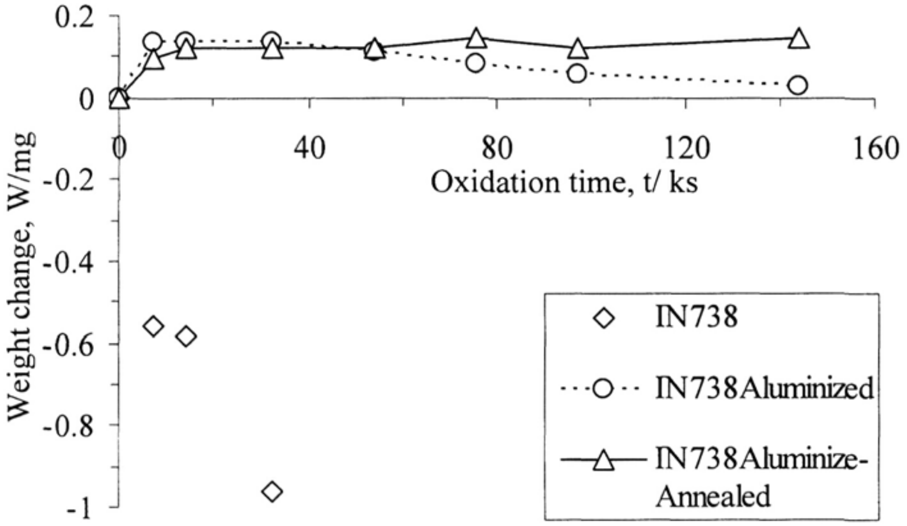

Fig. 6: Weight of samples after oxidation test at 1273 K under ambient atmosphere

layer was fine and uniform which is a preferable structure for oxidation resistance. A thickness of the coating layer of approximately 100 μm obtained from four hours of aluminizing should be adequate for improving the oxidation resistance of IN 738.

The coating layer can be annealed by heat treatment at 1273 K under argon atmosphere. After annealing the coated IN738 samples, the coating layer changed from Ni_2Al_3 to NiAl which has excellent oxidation resistance. After annealing for 21.6 ks (6 hours), the GIXD profiles show that the Ni_2Al_3 had changed to NiAl (see **Fig. 5**). When the annealing time was increased to 36 ks (10 hours), the relative intensities of NiAl peaks increased while the relative intensities of the Ni_2Al_3 peaks decreased. This implies that the amount of NiAl increased with increasing holding time for the annealing process.

The oxidation test showed that the oxidation resistance of IN738 was markedly improved by coating and annealing. The weight of as-cast IN738 decreased after oxidation testing for 7.2 ks (2 hours) due to the delamination of the oxide layer formed on the surface (see **Fig. 6**).

In contrast, the weights of the coated sample and coat-annealed samples slightly increased because of the formation of surface-oxide film which remained on the surface after oxidation testing for 144 ks. The explanation for the differences in oxidation resistance is that the coated and as-cast samples had a different type of surface oxide film. From GIXD profiles as shown in **Fig.7**, the surface-oxide film which formed on the top surface of the as-cast sample consisted mainly of a nickel-oxide film which could easily delaminate from the sample surface and, hence, could not act as a protective film. On the top surface of the coated and coat-annealed sample, aluminum-oxide film formed after oxidation testing since the nickel aluminide layer provided aluminum atoms to form the aluminium oxide film. This dense aluminum oxide film can be used as a protective layer by retarding oxygen diffusion, hence suppressing the oxidation process.

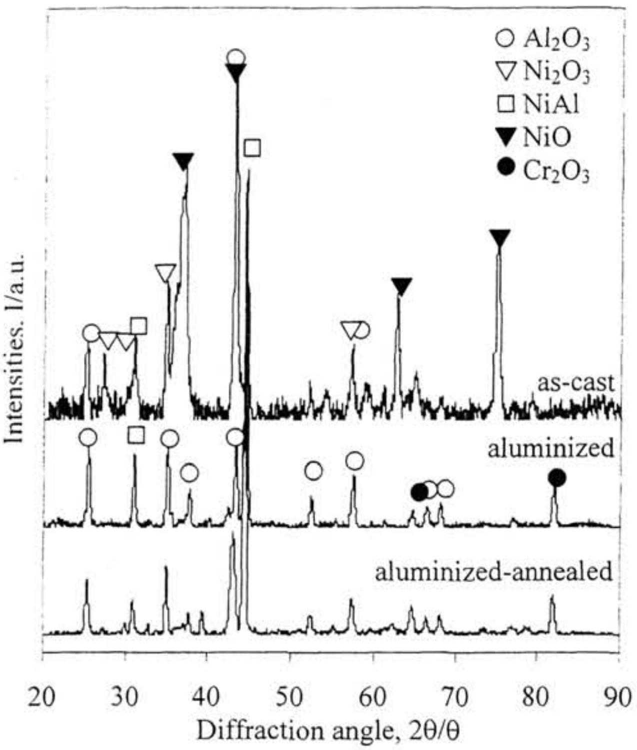

Fig. 7: GIXD profiles of IN738 after oxidation test at 1273 K for 54 ks under ambient atmosphere.

4. CONCLUSION

Pack aluminizing by using Al, Al_2O_3 and NH_4Cl powder with a weight ratio of 5:15:80 can successfully form nickel-aluminide film on IN738. The main phase of the coating layer was Ni_2Al_3 for low-temperature aluminizing at 1073 and 1173 K, while Ni_2Al_3 and $AlCr_2$ were found in the case of high-temperature aluminizing at 1273K. The growth rate of the nickel-aluminide layer increased with increasing temperature since the growth of the nickel-aluminide layer was controlled by diffusion, i.e., inward diffusion for low-temperature aluminizing and outward diffusion for high-temperature aluminizing. The annealing process under argon atmosphere is an appropriate process to homogenize the coating layer and form the NiAl phase to increase oxidation resistance. In this research, the optimum annealing condition was 1273 K for 36 ks. Oxidation resistance of IN738 was markedly improved by pack aluminizing and annealing.

ACKNOWLEDGEMENTS

The authors would like to express their gratitude to the Thailand Research Fund (TRF) for financially supporting this research under Contract Number MRG5080012.

REFERENCES

1. C.T. Sims and W.C. Hagel, *The Superalloys*, John Wiley & Sons, New York, (1987) p. 341-370.
2. M. J. Donachie and S. J. Donachie, *SUPERALLOYS: A Technical Guide*, ASM International, Ohio, (2002) p. 311-315.
3. B. Goswami, A. K. Ray and S. K. Sahay, *High. Temp. Mater. Process.* **23(2)**, 73-92 (2004).
4. T. Sournail, *Coating for turbine blades*, http//www.msm.cam.ac.uk, 2007
5. K. Das, M. Roy and V. Singh, *Mat. Sci. Tech.* **15**, 1199-1207 (1999).
6. C. Houngninou, S. Chevalier and J. P. Larpin, *App. Surf. Sci.* **236**, 256-269 (2004).
7. A. M. Hodge and D. C. Dunand, *Intermetallics* **9**, 581-589 (2009).
8. F. Shahriari, F. Ashrafizadeh and A. Saatchi, *J. Jap. Soc. of Heat Treat.* **49**, 209-212 (2009).