A Study of Oxidation Resistant Coating on TiAl alloys by Cr Evaporation and Pack Cementation

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A Cr+Al-type composite coating is applied to improve the properties of aluminide coating layers, $TiAl_3$, formed on TiAl alloys. This method is performed by Cr evaporation on the TiAl-XNb(X=1,6at%) substrate followed by pack aluminizing. The coating layer formed by the composite coating process consists of the outer layer of Al_4Cr and the inner layer of $TiAl_3$ regardless of the Nb content. However, these coating layers are transformed to $Ti(Al,Cr)_3$ layers with $L1_2$ structures during oxidation. In particular, as Nb content increases, the grain size of the inner $TiAl_3$ layer becomes smaller and the diffusion rate of Cr increases after oxidation. Faster formation of a $Ti(Al,Cr)_3$ layer with an $L1_2$ structure through Nb addition is more effective to improve cracking resistance at the beginning of oxidation of TiAl alloys. However, growth of $Ti(Al,Cr)_3$ formed on the coating layer becomes slower as the Nb content in the coating layer is increased. As a result, the addition of a large amount of Nb to composite coating layer is not desirable due to poor ductility of the coating layer. A Ti $(Al,Cr)_3$ layer with an $L1_2$ structure developed during oxidation showed much better ductility compared with other coating layers.

Keywords : aluminide coating, $TiAl_3$, $L1_2$-$Ti(Al,Cr)_3$, Cr evaporation

1. Introduction

Although there are many surface coating technologies available to improve oxidation resistance of TiAl alloy, pack cementation seems to be quite promising because it is a relatively simple process which provides reliable a the coating layer properties to facilitate oxidation resistance. The pack aluminizing of TiAl produces a $TiAl_3$ coating layer, and due to the sufficient amount of Al in the coating layer, stable Al_2O_3 is formed as it is exposed to a high temperature oxidation atmosphere.[1] However, the $TiAl_3$ coating layer formed on the TiAl alloy is quite brittle and thus, easily spalls with cracks under mechanical and thermal stresses during the aluminizing process and oxidation. Formation of such a brittle coating layer limits the improvement of oxidation resistance of the aluminized TiAl alloy.

Much work has been reported on the transformation of the crystal structure of $TiAl_3$ through the addition of ternary alloying elements to improve its ductility. Ternary alloying elements such as Ni, Fe, Cu, Mn, Ag, and Cr have been confirmed to change the crystal structure of $TiAl_3$ from low symmetry DO_{22} to high symmetry $L1_2$.

[2-6] Especially the $TiAl_3$ alloys containing Cr more than 8 at% were reported to have better compressive ductility than those alloyed with other ternary alloying elements.[5] Furthermore, due to the similarities between $Ti(Al,Cr)_3$ with $L1_2$ structure and TiAl alloys with $L1_0$ structure in crystal structure and lattice parameter,[6,7] growth stresses generated by lattice mismatches and volume differences between the coating layer and substrate may be reduced. Therefore, the formation of $Ti(Al,Cr)_3$ with $L1_2$ structures on TiAl substrate can be considered as quite desirable for minimizing defects formation in the coating layer during the aluminizing process and oxidation.

It is known that the addition of Nb to the aluminide coating layer, $TiAl_3$ causes grain refinement of the coating layer and also improves its ductility and oxidation resistance.[14] For further improvement of ductility of the aluminide layer, besides Cr, the addition of Nb to the aluminide layer is expected to be quite effective.

In this study, Cr is incorporated in the $TiAl_3$ coating by a Cr+Al-type composite coating performed by Cr evaporation on the TiAl-XNb(X=1,6at%) alloy substrates, followed by pack aluminizing. The purpose of this study is to elucidate the combined effect of Cr and Nb on the

properties of the aluminide coating layer formed on TiAl alloys with the addition of a small amount of Nb ternary element with respect to microstructure and mechanical property.

2. Experimental

2.1 Specimen preparation

The ingots produced by vacuum arc melting were homogenized at 1150°C for 72h in a vacuum quartz tube and then furnace cooled to room temperature. Each ingot was sliced to 10(13(2mm by an EDM (electrical-discharge-machining) and all sliced specimens were polished to No.1500 with SiC paper and ultrasonically cleaned in acetone. The substrate materials used in this study were TiAl and Ti-Al-XNb(X=1,6at%) alloys.

2.2 Cr+Al-type composite coating

For Cr evaporation, Cr source (purity 99.9%) was placed in a copper crucible and vaporized by heating with an electron-beam source. The initial vacuum level of the chamber and the substrate temperature were set at 10^{-5} torr and 360°C, respectively. The acceleration voltage of the electron beam was 10KV and the emission current was 80mA. The coating time was an hour to obtain a Cr layer with $10\sim15\mu m$ thickness. After Cr evaporation on TiAl alloy, all specimens were pack aluminized using a high activity process. For the pack process, 15 wt% of pure Al powder was used as a source metal, 3 wt% NH_4Cl powder as an activator, 82 wt% of Al_2O_3 powder as a filler material, and Ar gas as a carrier gas. The pack aluminizing process was carried out at 950°C for 6 hours.

2.3 Evaluation of the coating layer

For the analysis of microstructures and compositional distribution of the coating layer, OM (optical microscopy) and SEM (scanning electron microscopy) were used, respectively. Small precipitates in the coating layer were analyzed using FE-SEM (field emission scanning electron microscopy). Toughness of the coating layer was estimated using microhardness test. Evaluation of the oxidation resistance of the specimen was carried out by isothermal oxidation tests at 1000°C.

3. Results

For Fe and Ni-base superalloys, to ensure adequate resistance against hot corrosion, an aluminide coating should contain significant levels of Cr. Therefore, a pack cementation process which could deposit Cr and Al simultaneously has been developed. The success of this

codeposition method has been reported in several cases [8-10]. However, this codeposition process seems not to be applied to Ti-base alloys because of replacement reactions as listed below;

$$2CrCl_2(g) + Ti = 2Cr + TiCl_4(g) \quad \Delta G = -113.765(KJ/mol)$$

$$4CrCl_3(g) + 3Ti = 4Cr + 3TiCl_4(g) \quad \Delta G = -695.885(KJ/mol)$$

The equilibrium partial pressure of $TiCl_4(g)$ is high, indicating that loss of Ti from the substrate occurs to a significant extent during coating deposition. This was verified by pack cementation for a TiAl substrate in a NaCl-activated pack at 1100°C using Al-10%Cr master alloy. After the pack cementation process, a severe loss of substrate was observed. Therefore, it is thought that a two-step process is required for the addition of Cr into the aluminide coating layer formed on the TiAl. A Cr+Al composite coating has been prepared by Cr evaporation on the TiAl substrate followed by pack aluminizing.

3.1 Composite coating of TiAl alloy

Figure.1 shows the transformation of the composite coating layer formed on the TiAl specimen after isothermal oxidation at 1000°C. The identification of phases in the coating layer was confirmed from EDS data and ternary phase diagrams of Ti-Al-Cr systems in the literature.[11-13] Before oxidation, a composite coating layer was composed of two layers. The composition of the outer layer is very close to the Al_4Cr phase and the inner one $TiAl_3$. The top portion of the inner $TiAl_3$ layer contains a small amount of Cr. No detectable composition gradient across each layer was found. During the pack aluminizing process, Al atoms released from halides gas are deposited on the surface and diffuse into the Cr layer. The deposited Cr reacts mainly with diffused Al and forms intermetallic compound Al_4Cr. The amount of inward-diffused Cr into TiAl substrate seems to be very small. On the other hand, continuous inward diffusion of Al forms an inner intermetallic $TiAl_3$ layer. The growth of the coating layer occurrs mainly by inward diffusion of Al during pack aluminizing.

As shown in Figure 1 (a), the desired $Ti(Al,Cr)_3$ coating layer with $L1_2$ structure was not obtained by the two-stage coating process of Cr evaporation and pack aluminizing. However, the coating layers of Al_4Cr and $TiAl_3$ were transformed to $Ti(Al,Cr)_3$ by the interdiffusion of those elements during oxidation. After 50h oxidation, an outer layer of Al_4Cr was transformed to $Al_{17}Cr_9$ with small amount of Ti, and formation of Cr_2Al precipitates was observed in the $Al_{17}Cr_9$ layer. The Cr content in the $TiAl_3$ layer was increased up to 4at%. Also,a $TiAl_2$ layer was

Fig. 1. The microstructures of composite coating formed on TiAl during different oxidation time. (a)after coating, (b) 50 hours, (c) 100hours, (d) 200hours
① Al₄Cr, ② TiAl₃, ③ TiAl₂, ④ Al₁₇Cr₉, ⑤ Cr₂Al, ⑥ L1₂-Ti(Al,Cr)₃

formed at the interface of the substrate TiAl and TiAl₃ layer by the inward diffusion of Al and the outward diffusion of Ti. The compositional distribution of each layer after oxidation for 100 hours was similar to that after oxidation for 50 hours except for a small decrease in thickness of the Al₁₇Cr₉ layer and a small increase in thickness of the inner two layers. After oxidation for 200 hours, however, the amount of Cr in the Ti(Al,Cr)₃ layer was increased to 13at%. The composition of this layer was 27at% Ti, 60at% Al and 13at%Cr.1201

3.2 Composite coating of TiAl alloy with Nb

Figure.2 and 3 show the transformation of the composite coating layer formed on the TiAl-XNb(X=1,6at%) specimens after isothermal oxidation at 1000°C. The microstructure and compositional distribution of the coating layer transformed during oxidation seem to be similar to those of coating layers formed on TiAl. However, Nb addition affects diffusion of Al and Cr in the coating layer. After coating, the coating layer consists of the same two layers as those of TiAl whitout Nb addition but the grain size of the inner TiAl₃ is smaller than that of TiAl without Nb addition. In particular, the grain size of the inner TiAl₃ formed on TiAl-6Nb alloy is within a few micrometers. It is known that the addition of Nb refines grains of aluminide coating layers on TiAl alloy.[14]

This grain refinement has a particular effect on inward diffusion of Cr at the initial period of oxidation. In the case of TiAl alloy without Nb addition, even after 100h of oxidation, the amount of diffused Cr into the TiAl₃ layer is only 4at% and the formation of Ti(Al,Cr)₃ is not observed. However, in the case of TiAl alloy with Nb addition, after 50h oxidation, the formation of Ti(Al,Cr)₃

Fig. 2. The microstructures of composite coatings formed on TiAl-1Nb during different oxidation times (a)after coating, (b) 50 hours, (c) 100hours, (d) 200hours

Fig. 3. The microstructures of the composite coating formed on TiAl-6Nb during different oxidation times (a)after coating, (b) 50h hours, (c) 100hours, (d) 200hours
① Al₄Cr, ② TiAl₃, ③ TiAl₂, ④ TiAl₃+Ti(Al,Cr)₃ ppt, ⑤ Al₁₇Cr₉ ⑥ L12-Ti(Al,Cr)₃, ⑦ TiAl₃+Ti(Al,Cr)₃

① Al₄Cr, ② TiAl₃, ③ TiAl₂, ④ L1₂-Ti(Al,Cr)₃, ⑤ Al₁₇Cr₉ is observed. In cases of addition of 1at%Nb, as shown in Figure. 2(b), an L₁₂-Ti(Al,Cr)₃ layer with thickness of a few micrometers is formed after 50h of oxidation, and diffused Cr through grain boundary is also observed in the TiAl₃ matrix. That is, lattice and grain boundary diffusion of Cr are both observed. If the content of Nb is increased to 6at%, grain boundary diffusion of Cr becomes more dominant. As shown in Figure. 3(b), the fast inward diffusion of Cr through grain boundaries of TiAl₃ phase forms Ti(Al,Cr)₃ precipitates in the TiAl₃ matrix. Figure 4 shows a magnified secondary electron image of the composite coating layer formed on TiAl-6Nb after 50h oxidation. The black section shows Ti(Al,Cr)₃ precipitates and the gray section is the TiAl₃ matrix. It is clearly seen that Ti(Al,Cr)₃ is formed in the joint areas among grain boundaries after grain boundary diffusion of Cr, and the size is about 2~3μm. According to EDS analysis, the content of Nb incorporated in the TiAl3 matrix is about 2~3at% and Nb is not included in the

Fig. 4. Cross sectional secondary electron image of composite coating layer formed on TiAl-6Nb after 50h of oxidation

Ti(Al,Cr)$_3$. The fast inward diffusion of Cr into TiAl$_3$ can make the coating layer ductile by forming Ti(Al,Cr)$_3$ phase which prohibits microcrack formation and propagation. At this point, the appearance of Ti(Al,Cr)$_3$ in the coating layer formed on TiAl alloys with Nb addition even after 50h of oxidation is quite noticeable.

After 100h of oxidation, in the case of TiAl with addition of 1at% Nb, inward diffusion of Cr becomes a little blunt, and the growth of the Ti(Al,Cr)$_3$ layer formed after 50h of oxidation is not observed. Relatively dominant inward diffusion of Al increases the thickness of TiAl$_2$ layer. But the growth width of TiAl$_2$ is less than that of TiAl alloy without Nb. Through lattice diffusion of Cr, the average amount of Cr included in the TiAl$_3$ is about 4~5at% but not enough for the formation of L$_{12}$-Ti(Al,Cr)$_3$. On the other hand, in cases of TiAl with addition of 6at% Nb, the outer Al$_{17}$Cr$_9$ layer disappears after 100h of oxidation, and the L$_{12}$-Ti(Al,Cr)$_3$ layer with a thickness of a few micrometers is formed in the outer region of the coating layer. Below this layer, although not quite distinguished from the TiAl$_3$ layer with Ti(Al,Cr)$_3$ precipitates formed after 50h oxidation, a dual phase of TiAl$_3$ and Ti(Al,Cr)$_3$ is formed because lattice diffusion of Cr from the grain boundaries of the TiAl$_3$ layer causes growth of Ti(Al,Cr)$_3$ precipitates. According to FESEM analysis, the ratio of TiAl$_3$ and Ti(Al,Cr)$_3$ is about 4:1. It is found that Nb is not still incorporated with Ti(Al,Cr)3 phase but maintains its original composition in the TiAl$_3$. In addition, the growth width of TiAl$_2$ is quite small, which is consistent with previous research.[14]

After 200h of oxidation, in the case of TiAl with addition of 1at% Nb, continuous L$_{12}$-Ti(Al,Cr)$_3$ with a thickness of more than 20μm is formed although the Al$_{17}$Cr$_9$ and TiAl$_3$ layers remain. The average composition of L$_{12}$-Ti(Al,Cr)$_3$ is 25at%Ti+64at%Al+11at%Cr. The composition of 25Ti-64Al-11Cr belongs to the L$_{12}$ phase field in the ternary phase diagram. But in the case of TiAl with addition of 6at% Nb, continuous L$_{12}$-Ti(Al,Cr)$_3$ is not yet formed although portion of this phase is increased to 30vol% in the TiAl$_3$+Ti(Al,Cr)$_3$layer. For the growth of the TiAl2 layer due to inward diffusion of Al, TiAl with addition of 1at% Nb shows a continuous increase and almost half of the coating layer is occupied with TiAl$_2$. However, in the case of TiAl with addition of 6at% Nb, the growth width of TiAl$_2$ is still small.

In summary, TiAl with addition of 6at%Nb shows faster inward diffusion of Cr into the TiAl$_3$ layer than TiAl with the addition of 1at%Nb at the initial period of oxidation. This is mainly due to finer grains of TiAl$_3$ layer formed on TiAl alloy with the addition of 6at%Nb. However, during oxidation, growth of Ti(Al,Cr)$_3$ formed on the grain boundaries is slower as the content of Nb is increased.

3.3 Evaluation of mechanical properties of the composite coating layer

To evaluate the mechanical properties of each layer formed after composite coating, a Vickers microhardness test was performed. The measured value of each layer is listed in Table 1 and is roughly consistent with that mentioned in the literature.[5,11] The hardness value of bulk L1$_2$-type Ti$_{25}$Al$_{67}$Cr$_8$ in the literature was 151(Hv). The difference between the measured value and that reported

Table 1. Hardness value of each layer of composite coating (TiAl without Nb addition)

Coating layer	H_v(DPH)	Remarks
Al₄Cr(100g, 10sec)	439.2(±20)	
TiAl₃(100g, 10sec)	433.3(±20)	
TiAl(100g, 10sec)	255(±20)	
TiAl₂(100g, 10sec)	347.4(±20)	
Al₁₇Cr₉(50g, 10sec)	501.4	Microcrack formation for even 50g, not easy for measurement for small size.
Ti(Al, Cr)₃ (10g, 10sec)	172.8(±10)	

value by Nic etc. resulted from both experimental error and the difference in specimen preparation. However, this error was thought to be comparable. The Ti(Al,Cr)₃ coating layer shows the lowest value and therefore the best ductile structure among other layer. From this point of view, it is recognized that the Ti(Al,Cr)₃ layer has a cubic L1₂ structure which is a most desirable structure for improvement of ductility of the coating layer.

4. Disccusion

4.1 Effects of Cr and Nb on ductility of TiAl₃ layer

In this study, Cr is incorporated in the TiAl₃ coating by Cr+Al-type composite coating which was performed by Cr evaporation on TiAl-XNb(X=1,6at%) alloy substrates followed by pack aluminizing. The coating layer formed by the composite coating process consists of the outer layer of Al₄Cr and the inner layer of TiAl₃ regardless of Nb content. However, composite coating layers are transformed to an Ti (Al,Cr)₃ layer with an L1₂ structure during oxidation. Composite coating layer formed on TiAl alloy without addition of Nb is transformed to a continuous L1₂-Ti(Al,Cr)₃ layer after 200h of oxidation, although the inward diffusion of Cr is not dominant and the formation of L1₂-Ti(Al,Cr)₃ is not observed even after 100h of oxidation. On the other hand, a composite coating layer formed on TiAl alloy with Nb shows the appearance of L1₂-Ti(Al,Cr)₃ in the coating layer after 50h of oxidation. This is mainly due to grain refinement of the TiAl₃ layer through Nb addition and faster inward diffusion of Cr through grain boundaries. The fast inward diffusion of Cr into TiAl₃ can make the coating layer ductile by forming Ti(Al,Cr)₃ phase and prohibits microcrack formation and propagation. At this point, Nb addition is more effective for improving the ductility of the coating layer at the initial time of oxidation. However, the growth rate of Ti(Al,Cr)₃

formed at the beginning of oxidation becomes slower as the content of Nb incorporated into TiAl₃ is increased. In the case of no addition of Nb and 1at% addition of Nb to TiAl alloy, after 200h of oxidation, continuous L1₂-Ti(Al,Cr)₃ is formed and the amount of Nb included in TiAl₃ during oxidation is below 0.5at%. In case of 6at% addition of Nb, the content of Nb incorporated to TiAl₃ during oxidation is 2~3at% and continous L1₂-Ti(Al,Cr)₃ is not formed even after 200h of oxidation. As the portion of Ti(Al,Cr)₃ is increased, the ductility of the coating layer is increased. In the end, considering only ductility of coating layer, the effect of the addition of Nb on the composite coating layer is detrimental.

4.2 Degradation of composite coating layer

Nb addition prohibits degradation of coating layers during oxidation. The coating layer formed on the TiAl-XNb alloys by composite coating is degraded by inward diffusion of Al. Particularly, in the case of TiAl alloy without Nb addition, after 200h of oxidation, the TiAl₂ layer occupies half of the coating layer. But as Nb content is increased, the growth of the TiAl₂ layer is suppressed. Nb, remaining in the TiAl₃ layer instead of being incorporated into Ti(Al,Cr)₃ during continuous oxidation, forms η-(Nb,Ti)Al₃ phase after 200h of oxidation. Figure. 5 shows a cross sectional secondary electron image of a composite coating layer formed on TiAl-6Nb after 200h of oxidation. The numerous white particles observed in the gray background phase of TiAl₃ contain 7-8at% of Nb although the average Nb content contained in the coating layer is only 2-3at%. The average composition of this part is 22at%Ti+70at%Al+8at%Nb and belongs to the η-(Nb,Ti)Al₃ phase field.[18] The content of Cr in this part is quite small. Nb present in the TiAl₃ coating layer seems to inhibit the grain growth and inward diffusion of Al by the formation of (Nb, Ti)Al₃ during oxidation. However,

Fig. 5. Cross sectional secondary electron image of composite coating layer formed on TiAl-6Nb after 200h oxidation

More research is required to elucidate a clear understanding of the mechanism of the Nb effect on degradation of the coating layer.

$L1_2$-Ti(Al,Cr)$_3$ phase, which is reported to have better compressive ductility than that alloyed with other ternary alloying elements,[5] is degraded by inward diffusion of Al into TiAl substrate.[19] The Nb-added TiAl$_3$ layer shows a higher hardness value than $L1_2$-Ti(Al,Cr)$_3$, but, by surpressing inward diffusion of Al into substrate, the Nb-added TiAl$_3$ layer can increase the performance life of coating layer. Therefore, considering both ductility and performance life, the coating layer consisting of $L1_2$-type Ti(Al,Cr)$_3$ and DO_{22}-type TiAl$_3$ with an adequate amount of Nb in the coating layer seems to be most desirable for oxidation resistance. However, a further study is required to determine the optimum amount of Nb addition in the coating layer.

5. Conclusions

A Cr+Al-type composite coating was applied to improve the properties of the aluminide coating layer, TiAl$_3$ formed on TiAl alloys. This method was performed by Cr evaporation on the TiAl-XNb(X=1,6at%) substrate followed by pack aluminizing.

1. The coating layer formed by the composite coating process consists of an outer layer of Al$_4$Cr and an inner layer of TiAl$_3$ regardless of Nb content. However, these coating layers are transformed to Ti (Al,Cr)$_3$ layers with $L1_2$ structures during oxidation.

2. The addition of Nb refines grains of the aluminide coating layer on TiAl alloy. This grain refinement causes faster formation of Ti(Al,Cr)$_3$ by rapid inward diffusion of Cr through TiAl$_3$ layer grain boundaries in the initial period of oxidation. However, the growth of Ti(Al,Cr)$_3$ formed on the coating layer is slower as the content of Nb in the coating layer is increased. As a result, the addition of a large amount of Nb to the composite coating layer is not desirable due to poor ductility of the coating layer.

3. A Ti(Al,Cr)$_3$ layer with an $L1_2$ structure developed

during oxidation showed much better ductility than other coating layers.

4. The coating layer formed on TiAl-XNb alloys with a Cr+Al composite coating is degraded by the inward diffusion of Al. But as the content of Nb is increased, degradation of the coating layer is prohibited by suppressing the growth of the TiAl$_2$ layer.

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