

## INVESTIGATION ON MICROSTRUCTURE AND OXIDATION BEHAVIOR OF Cr-MODIFIED ALUMINIDE COATING ON $\gamma$ -TiAl ALLOYS

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Microstructure and oxidation behavior of aluminide coating has been investigated. The layers were examined by optical microscopy, scanning electron microscopy (SEM) equipped with EDS and X-ray diffraction method. The isothermal oxidation behaviors of samples were investigated at 950°C for 200 h. The results indicated that TiAl<sub>3</sub> were formed on substrate. In addition, aluminide coating improved the oxidation resistance of  $\gamma$ -TiAl alloys by forming a protective alumina scale. Moreover, during oxidation treatment the interdiffusion of TiAl<sub>3</sub> layer with  $\gamma$ -TiAl substrate results in depletion of aluminum in the TiAl<sub>3</sub> layer and growth of TiAl<sub>2</sub> layer. After oxidation treatment the coating layer maintained a microstructure with phases including TiAl<sub>3</sub>, TiAl<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.

**Keywords:** *aluminide coating, pack cementation,  $\gamma$ -TiAl, oxidation behavior.*

The  $\gamma$ -TiAl intermetallic compounds have low density and excellent strength and modulus retention properties at high temperatures up to 800°C [1]. They offer enormous potential in critical strength application areas for aerospace and power industries where high specific strength and stiffness are required. However, in order to fully apply their potentials, efficient and effective technologies must be developed to ensure their long-term mechanical and structural integrity in oxidative and corrosive environments at high temperatures.

Titanium aluminide alloys suffer poor oxidation resistance that limits their industrial applications at high temperatures. To improve the oxidation resistance of TiAl intermetallic compounds at high temperatures, several surface modification technologies have been investigated such as aluminizing [2–4], MCrAlY overlay coatings [5–6], ceramic coatings [7–8] and pre-oxidizing at low oxygen pressure [9–11].

Pack aluminizing is used as a coating method for high temperature alloys because of its practical advantages than other coating methods. The pack aluminizing of TiAl basically produces TiAl<sub>3</sub> coating.

In this paper, microstructures of aluminide coatings have been evaluated. Further oxidation tests have been performed on aluminide coating for  $\gamma$ -TiAl alloy substrate at 950°C.

**Experimental procedures.** The high purity elements were accurately weighed and melted on a water cooled copper mold, in a vacuum arc remelting furnace using a non-consumable W electrode to prepare samples of Ti–47Al and Ti–47Al–2Cr (at.%) alloys. The alloy was kept molten for 2 min, allowed to cool, turned and melted again. This process was repeated at least five times in order to ensure homogeneity.

Specimens were fine polished using № 1500 SiC-grit papers before pack cementation. The components in pack cementation include 15 wt.% Al + 4 wt.% NH<sub>4</sub>Cl + 81 wt.% Al<sub>2</sub>O<sub>3</sub> fine mixed powders. Specimens were weighted and embedded in the pack mixture. The pack cementation process is performed at 950°C for 6 h. To prevent

oxidizing the Ar–H<sub>2</sub> atmosphere was used during pack cementation process. Oxidation tests were conducted at 950°C in tube furnace at room atmosphere. Weight changes were measured with a precision electronic balance with 1·10<sup>-4</sup> g accuracy. Microstructure of treated samples assessed by optical microscope and SEM (model philips-XL30) image observations. EDX elemental analysis was used as well as X-ray diffraction (XRD) (model philips X’pert) for phase analysis. SEM instrument was equipped with an energy dispersive X-ray spectrometer (EDS). XRD method used Cu–K<sub>α1</sub> radiation with  $\lambda = 0.154056$ .

**Results and Discussions. Microstructure assessment of aluminide coating.** Cross-section optical micrographs of aluminide coatings on TiAl and TiAlCr alloys are shown in Fig. 1. The coating layers were identified by XRD as TiAl<sub>3</sub> for both TiAl and TiAlCr specimens. The results of XRD pattern are similar and shown in Fig. 2a. It can be clearly seen that the main phase of the coatings is TiAl<sub>3</sub>. In TiAl specimens a TiAl<sub>3</sub> layer with approximately 65  $\mu\text{m}$  of thickness formed on the surface and the cracks formed through the grain boundaries. Besides some parts of TiAl<sub>3</sub> layer, formed on TiAl specimens, fragmented after pack aluminizing. In contrast, the TiAl<sub>3</sub> layer which was formed on TiAlCr alloy has much fewer cracks than the formed layer on TiAl alloy. It is evident that the coating consists of a TiAl<sub>3</sub> layer with the thickness of 76  $\mu\text{m}$  after 6 h of deposition at 950°C. Since there are not any pack filler particles (Al<sub>2</sub>O<sub>3</sub>) in the coating, this implies that the coating was formed by the inward growth mechanism. It seems that adding Cr element to TiAl alloy will lead to the formation of aluminide coating with fewer cracks. Zhou et al. [12] show that addition of Cr to  $\gamma$ -TiAl intermetallic alloy prevents the formation of cracks in the coating and so improves the coating toughness which is in a good agreement with the results of this study. The grain size of the TiAl<sub>3</sub> layer formed on TiAlCr alloy is finer than that formed on TiAl alloy. Since grain boundaries act as fast diffusion paths for Al during pack aluminizing [13], the growth rate of TiAl<sub>3</sub> layer is higher as the grain size decreased. Thus, the TiAl<sub>3</sub> layer formed on TiAlCr alloy has smaller grain size which shows the thicker TiAl<sub>3</sub> layer.

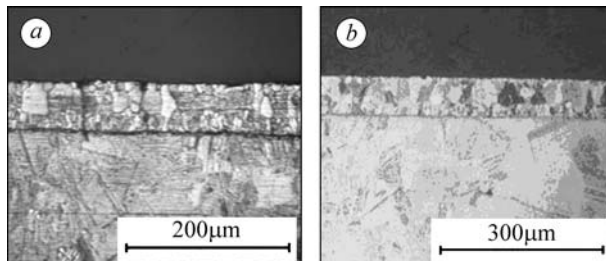


Fig. 1. Microstructure of aluminide coating on Ti–47Al (a) and Ti–47Al–2Cr (b) with the average size of grains of 123  $\mu\text{m}^2$  (a) and 187  $\mu\text{m}^2$  (b).

Aluminide coating is one of the attractive candidate coatings for applying at high temperatures. The TiAl<sub>3</sub> layer which is formed on TiAl intermetallic alloy has good oxidation resistance, but it suffers greatly from brittleness at ambient temperature because of its low symmetry tetragonal DO<sub>22</sub> structure. Other investigations show that one of the effective ways for improvement of the brittleness of TiAl<sub>3</sub> coating is the adding of ternary element such as Cu, Ni, Cr, ... more than 5 at.% into the substrate alloy [14]. It seems that by addition the mentioned element to the TiAl alloys the toughness of aluminide coating improves by transformation of the DO<sub>22</sub> structure to the cubic L<sub>12</sub> structure. It results from the above that reducing of microcracking propensity is related to improvement of coating toughness. Furthermore it has been seen in this investigation that the microstructure of TiAl<sub>3</sub> layer that was formed on TiAlCr alloy is finer than that of TiAl<sub>3</sub> formed on TiAl. Grain refinement can improve toughness by reducing the slip length and stress concentration. This may result in more homogeneous deformation by multiple slip in the vicinity of grain boundaries. Thus beside the phase transformation

as mentioned above, grain refinement can lead to increasing of toughness and then decreasing of cracking propensity.

In general, the addition of ternary element increased the toughness of the coating layer formed on TiAl. These results are in good agreement with the number of cracks formed in the TiAl<sub>3</sub> layer, as shown in Fig. 1. From these results, it is clear that the ternary element added to TiAl affects the mechanical properties of the coated layer and consequently affects the oxidation behavior of aluminized TiAl.

The TiAl<sub>3</sub> phase has a tetragonal DO<sub>22</sub> structure which has low symmetry and thus offers poor ductility and toughness [14]. Previous studies demonstrated that some alloying elements such as Nb, Cr, Cu, Ni, Fe and Mn can improve the ductility and toughness of TiAl<sub>3</sub> through change of the TiAl<sub>3</sub> structure to cubic L<sub>12</sub> type. In addition, aforementioned alloying elements can also enhance slip of systems at high temperature and increase the ductility of TiAl<sub>3</sub> [15, 16]. In the present study, addition of Cr into TiAl, clearly improves the toughness of the coatings, possibly by modifying or at least partial modifying the crystal structure and partial grain refinement of the TiAl<sub>3</sub> coating layer. As a result, by addition of Cr as alloying elements in TiAl alloy, probability of crack formation on protective aluminide coating after aluminizing process would be decreased and thus oxidation along the cracks will be suppressed efficiently. Therefore, as seen in Fig. 3, the aluminide coating formed on TiAl alloy containing Cr has better oxidation resistance than pure TiAl alloy.

**Oxidation Behavior.** To evaluate the oxidation resistance of aluminide coatings, isothermal oxidation tests were carried out on TiAl and TiAlCr and uncoated TiAlCr specimens at 950°C for 200 h. The plots of weight change per unit area versus time for different specimens at 950°C are shown in Fig. 3. It can be clearly seen that TiAlCr alloy without any coating has linear oxidation behavior at 950°C and a large amount of weight loss in this case is caused by spallation. The poor oxidation behavior of  $\gamma$ -TiAl alloys in air is commonly referred to the nitrogen effect. Dettenwanger et al. [17] and Rakowski et al. [18] proposed that inability of binary  $\gamma$  alloys to establish a continuous and protective, slowly growing Al<sub>2</sub>O<sub>3</sub> scale at 900°C in air is related to the formation of TiN during the initial stages of oxidation. The presence of TiN was postulated to interrupt the establishment of a continuous alumina scale. As oxidation proceeds, TiN is subsequently oxidized to form fast-growing nonprotective TiO<sub>2</sub>.

On the other hand, the specimens with the TiAl<sub>3</sub> protective layer have logarithmic oxidation manner. Using this kind of coating the better oxidation behavior of coated TiAlCr alloy than uncoated alloy is obtained (Fig. 3). Also it can be seen from Fig. 3

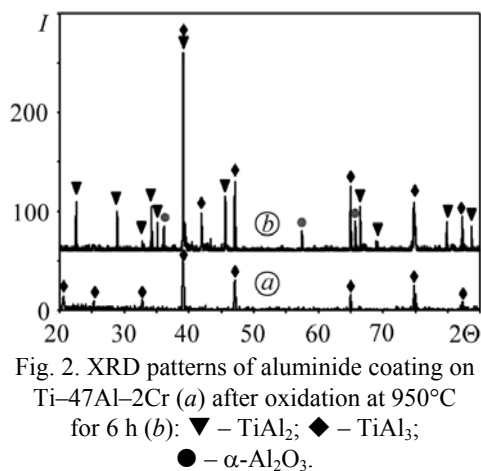


Fig. 2. XRD patterns of aluminide coating on Ti-47Al-2Cr (a) after oxidation at 950°C for 6 h (b):  $\nabla$  – TiAl<sub>2</sub>;  $\blacklozenge$  – TiAl<sub>3</sub>;  $\bullet$  –  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

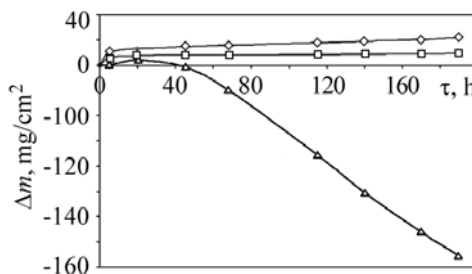


Fig. 3. Changes in mass change with oxidation time of bare TiAl and aluminide coated TiAl alloy in air at 950°C:  $\circ$  – TiAl/Aluminize;  $\square$  – TiAlCr/Aluminize;  $\triangle$  – TiAlCr.

that the coated TiAlCr behaves better than TiAl coated specimen and it has the less weight gain.

**Microstructure after oxidation.** The cross section microstructure of the aluminide layer and EDS analysis of aluminized microstructure after 200 h oxidation at 950°C is illustrated in Fig. 4. It can be clearly seen that 4 layers were formed after oxidation treatment on TiAlCr alloy. The results of EDS analysis confirm that the outermost layer is Al<sub>2</sub>O<sub>3</sub>. It seems that by outward diffusion of Al from initial TiAl<sub>3</sub> layer and its oxidation, the Al<sub>2</sub>O<sub>3</sub> layer has been formed. Outward diffusion of Al from TiAl<sub>3</sub> layer causes establishment of TiAl<sub>2</sub> layer under Al<sub>2</sub>O<sub>3</sub> layer. Other investigations confirm that Al<sub>2</sub>O<sub>3</sub> can form on the aluminide coating on γ-TiAl [1].

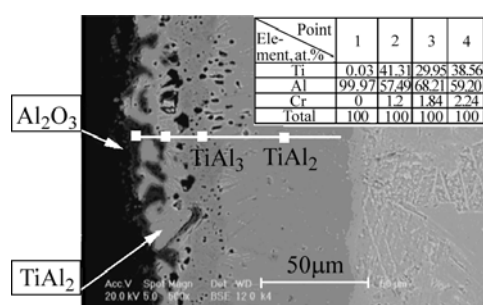
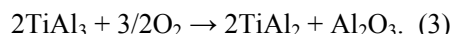


Fig. 4. Microstructure of aluminide coating and EDS analysis after 200 h oxidation at 950°C.

Addition of some alloying elements as Cr and Nb can decrease the volume amount of unfavorable TiAl<sub>2</sub> layer during oxidation test by reducing Ti activity [12]. On the other hand, a thin layer of Al<sub>2</sub>O<sub>3</sub> was formed on the outer region. It causes a depletion of aluminum in the adjacent TiAl<sub>3</sub> layer and brings about the formation of TiAl<sub>2</sub> phase with lower aluminum content at Al<sub>2</sub>O<sub>3</sub>-TiAl<sub>3</sub> interface according to the following reaction:



From the other point of view, it seems that inter-diffusion between TiAl and TiAl<sub>3</sub> phases at high temperatures results in formation of TiAl<sub>2</sub> layer. It appears that the below reaction can be the main reason of the TiAl<sub>2</sub> layer formation:



The XRD pattern of aluminide coating after oxidation is demonstrated in Fig. 2b. It verifies the EDS analysis and shows that Al<sub>2</sub>O<sub>3</sub>, TiAl<sub>2</sub> and TiAl<sub>3</sub> exist after oxidation.

## CONCLUSION

The TiAl alloy was Al-diffusion treated at temperature 950°C and the coated alloys were oxidized in air at 950°C for up to 200 h. The obtained results can be summarized as follows.

Aluminum diffusion treatment at 950°C for 6 h results in the formation of a coating consisting of the TiAl<sub>3</sub> layer of 65 μm thickness on TiAl alloy and 76 μm thickness on TiAlCr alloy. Addition of Cr as ternary element in γ-TiAl alloy may give the formation of a ductile aluminide coating and reduction of its microcracking propensity. The TiAl<sub>3</sub> coating greatly improves the oxidation behavior of TiAlCr alloy (more than 7 times) at 950°C for 200 h as compared with the uncoated TiAlCr alloy. The TiAl<sub>2</sub> layer was formed during oxidation tests due to the inter-diffusion between the TiAl substrate and TiAl<sub>3</sub> coating. Also this phase has been observed in the interface of Al<sub>2</sub>O<sub>3</sub> layer and TiAl<sub>3</sub>.

**РЕЗЮМЕ.** Досліджено мікроструктуру алюмінідного покриття та його поведінку під час високотемпературного окислення. Шари алюмінідів титану вивчали за допомогою оптичної мікроскопії, сканівної електронної мікроскопії (SEM) з використанням дисперсного рентгеноспектрометра (EDS) та рентгенівським дифракційним методом. Випробування проводили при 950°C впродовж 200 h. Встановлено, що на підкладці з титанового сплаву утворився TiAl<sub>3</sub>. Покриття з алюмініду титану покращує стійкість до окислення

сплавів з  $\gamma$ -TiAl, утворюючи захисну плівку з оксиду алюмінію. Під час окислення дифузійна взаємодія TiAl<sub>3</sub> з підкладкою  $\gamma$ -TiAl спричиняє зменшення кількості алюмінію у шарі TiAl<sub>3</sub> та збільшення шару TiAl<sub>2</sub>. Після окислення в покриві утворюється мікроструктура з фазами, що містять TiAl<sub>3</sub>, TiAl<sub>2</sub> та Al<sub>2</sub>O<sub>3</sub>.

**РЕЗЮМЕ.** Исследовано микроструктуру алюминидного покрытия и его поведение при высокотемпературном окислении. Слои алюминиды титана изучали с помощью оптической микроскопии, сканирующей электронной микроскопии (SEM) с использованием дисперсного рентгеноспектрометра (EDS) и рентгеновским дифракционным методом. Испытания проводили при 950°C в течение 200 h. Установлено, что на подкладке из титанового сплава образовался TiAl<sub>3</sub>. Покрытие из алюминиды титана улучшает стойкость к окислению сплавов из  $\gamma$ -TiAl, образуя защитную пленку из оксида алюминия. Во время окисления диффузионное взаимодействие TiAl<sub>3</sub> с подкладкой  $\gamma$ -TiAl влечет уменьшение количества алюминия в слое TiAl<sub>3</sub> и увеличение слоя TiAl<sub>2</sub>. После окисления в покрыве образуется микроструктура с фазами, которые содержат TiAl<sub>3</sub>, TiAl<sub>2</sub> и Al<sub>2</sub>O<sub>3</sub>.

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