RAPID PUBLICATION

Protectiveness of a CVD- Al_2O_3 Film on TiAl Intermetallic Compound against High-Temperature Oxidation

Shigeji Taniguchi*, Toshio Shibata* and Katsuhiko Takeuchi**

TiAl coupon specimens coated with Al_2O_3 films by a CVD technique were oxidized in a flow of purified oxygen at atmospheric pressure for 100 ks at 1073, 1173 and 1273 K. The mass gains due to the oxidation were negligible. The CVD Al_2O_3 films of about 3 μm thickness were protective and very adherent to the substrate even after the oxidation at all the temperatures tested except 1273 K. Irregularly shaped Al_2O_3 crystals grew on the specimen at 1273 K even though they were very small, showing a limited protection at this temperature.

(Received January 9, 1991)

Keywords: CVD- Al_2O_3 , TiAl, oxidation resistance, high temperature, protectiveness

The present article describes an excellent protectiveness of an Al_2O_3 film formed on a TiAl coupon specimen by a chemical vapor deposition (CVD) technique against high-temperature oxidation. The mass gains of the TiAl specimens coated with the CVD Al_2O_3 films of about 3 μm thickness due to the oxidation at 1073, 1173 and 1273 K for up to 100 ks are negligible.

The intermetallic compound TiAl is of considerable interest because of its high specific strength⁽¹⁾⁽²⁾ at high temperatures and hence its potential application to air-plane engine parts. However, the resistance of TiAl to high-temperature oxidation is very poor. It was found⁽³⁾⁻⁽⁶⁾ quite difficult to form a protective Al_2O_3 layer on it by a simple oxidation process in spite of its high Al content. Therefore, a few attempts, including preoxidation⁽⁷⁾ at low oxygen pressures and aluminizing⁽⁸⁾⁽⁹⁾, have been performed to enhance the formation of protective alumina layers. However, successful results have not yet been reported.

The TiAl coupon specimens used in the present study were cut out of an ingot, the chemical composition of which is shown in Table 1. The specimens having a size of about 15 × 10 × 1 mm were abraded with a series of SiC polishing papers of up to #1000. They were further polished to a mirror finish on a polishing cloth im-

pregnated with alumina powders of 0.3 μm in size. After polishing they were washed ultrasonically in baths of acetone and alcohol.

An apparatus similar to that used by Kim *et al.*⁽¹⁰⁾ was used for the deposition of Al_2O_3 films. A single specimen was hung with a thin Pt wire in a vertical reaction tube of transparent quartz so that it can be heated by an infrared-ray image furnace without heating the tube wall so high. When the specimen was heated in a hydrogen atmosphere to 1173 K, the atmosphere was changed to a mixture of CO_2 and H_2 both flowing at a rate of 16.5 $\text{ml} \cdot \text{s}^{-1}$ for 600 s to preoxidize the specimen slightly. The mass gain due to the preoxidation was very small such as 2 $\text{g} \cdot \text{m}^{-2}$ with the specimen surface showing slightly tarnishing color. The preoxidation was found to improve the adherence of the Al_2O_3 film to the substrate. However, the details of the influence of preoxidation are excluded here.

After the preoxidation gas mixtures of AlCl_3 and H_2 , and CO_2 and H_2 were introduced to the reaction tube through two gas lines to start the deposition at 1173 K for 3.6 ks. The total pressure in the reaction tube was maintained to about 50 kPa by adjusting a needle valve and operating a vacuum pump. The gas flow rates were controlled to the values which were reported⁽¹¹⁾ to give a highest deposition efficiency. After the deposition the specimen was cooled to room temperature in a hydrogen atmosphere. Further details on the deposition conditions and procedures have been reported elsewhere⁽¹²⁾⁽¹³⁾.

The isothermal oxidation tests were carried out in a flow of purified oxygen at atmospheric pressure using an auto-recording thermobalance.

Standard metallographic examinations were performed for the specimens before and after the oxidation with X-ray diffractometry (XRD) using $\text{Cu-K}\alpha$ radiation at 40 kV and 30 mA, scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX).

Table 1 Chemical composition of the TiAl specimen (mass %).

Al	Ti	Fe	C	H	O	N
37.8	Bal.	0.010	0.006	0.002	0.044	0.011

* Department of Materials Science and Processing, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565, Japan.

** Undergraduate Student, Osaka University. Present address: Nihon Denso Co. Ltd., 1-1 Shohwa-cho, Kariya, Aichi 448, Japan.

Fig. 1 Outer surface (a) and fractured edge (b) of the TiAl specimen coated with a CVD Al_2O_3 film (b, center), showing an almost uniform thickness and good adherence to the substrate (b, left).

Fig. 2 Oxidation curves of the TiAl specimens coated with the CVD Al_2O_3 films and without the coating.

Figure 1(a) and (b) show the outer surface and fractured edge respectively of the specimen coated with the Al_2O_3 film deposited at 1173 K for 3.6 ks. The substrate was completely covered with the film, cf. Fig. 1(a). The film seems dense under SEM at magnifications of up to $\times 10000$. The Al_2O_3 film, center in Fig. 1(b), is of almost uniform thickness and in complete contact with the substrate.

As far as the XRD showed the film consisted of $\alpha\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$. After the oxidation the peaks in XRD charts corresponding to $\alpha\text{-Al}_2\text{O}_3$ predominated, indicating the change to $\alpha\text{-Al}_2\text{O}_3$ taking place.

The kinetic results are summarized in Fig. 2. Here, $\Delta m \cdot A^{-1}$ means the mass gain per specimen area and t the oxidation time. The curve for the specimen without coating is also shown for reference. It is noteworthy that the mass gains of the coated specimens due to the oxida-

tion are negligible for up to 100 ks at all the temperatures tested. The excellent protectiveness of the CVD Al_2O_3 film can be understood in this figure.

Figure 3(a) and (b) show typical features of the outer surface and fractured edge respectively of the specimen oxidized at 1073 K for 100 ks. There is no significant structural change in the corresponding figures in Figs. 1 and 3. The CVD Al_2O_3 film (top layer in Fig. 3(b)) remains unchanged and there is no sign of the oxide formation on the outer surface or in the fractured edge. The specimens oxidized at 1173 K showed similar features under the SEM.

On the other hand, the Al_2O_3 film spalled locally during cooling after the oxidation at 1273 K for 100 ks as shown in Fig. 3(c). This indicates a limited protection of the film. Figure 3(d) is an area in (c) at a higher magnification, showing the growth of irregular shaped crystals.

The EDX showed that the metallic elements in them were 95 at.% Al and 5 at.% Ti, indicating the predominant diffusion of Al through the film to form Al_2O_3 crystals containing small amount of Ti. Therefore, the protection by the film at this temperature seems to be limited, even though the mass gain is negligible as shown in Fig. 2.

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Fig. 3 Outer surface (a) and fractured edge (b) of the coated specimen oxidized at 1073 K for 100 ks. The Al_2O_3 film (top layer in (b)) remains unchanged and no sign of oxidation in the substrate. Outer surface (c) of the coated specimen oxidized at 1273 K for 100 ks, showing partial spallation. (d) A high magnification of an area in (c), showing the growth of Al_2O_3 crystals of irregular shapes.

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