Protectiveness of CVD Al_2O_3 Films on TiN against High-Temperature Oxidation*

By Shigeji Taniguchi**, Toshio Shibata** and Akira Okada***

TiN coupons coated with Al_2O_3 films of about $2.6\text{ }\mu\text{m}$ formed by a chemical vapor deposition technique were oxidized in a purified oxygen flow at atmospheric pressure in a temperature range 1073 to 1273 K. The film is protective at 1073 K for at least up to 185 ks. Though the film decreases the oxidation rate at the other temperatures, it shows breakaway kinetics. The time before breakaway, t_b , increases as the film thickness increases, while it decreases as the oxidation temperature increases. During the oxidation a small number of rutile aggregates grow on the film, while porous massive rutile grows under the film. The mass gain due to the oxidation after t_b corresponds mainly to the growth of the massive rutile, implying enhanced transport of oxygen into the substrate. The oxidation rate is higher than that of alloys which form $\alpha\text{-Al}_2\text{O}_3$ scales as a rate-limiting layer. This difference is explained in terms of structural changes. A possible reason for the breakaway is also given in terms of the formation of gaseous products, such as nitrogen and nitrogen oxide, which can introduce mechanical defects in the film.

(Received October 23, 1989)

Keywords: CVD, Al_2O_3 , TiN, oxidation, high temperature, breakaway

I. Introduction

Chemical vapor deposition (CVD) techniques⁽¹⁾ have often been used for producing various ceramic coatings covering substrates of different shapes. One of the major applications of thin Al_2O_3 films formed by CVD methods is to coat cutting tools⁽²⁾ with the films to improve their lives and the surface finish of the work.

On the other hand, the application of the film as a protective coating against the oxidation or corrosion at high temperatures seems quite promising and hence very important. The number of such trials⁽³⁾ is, however, quite small.

The present study deals with the oxidation behavior of TiN coupons coated with CVD Al_2O_3 films to examine the applicability of the films as a coating material serving at high temperatures.

TiN is also a promising material having high specific strength and relatively high electrical conductivities at high temperatures, provided that its resistance to the attack by the environment, e.g., oxidation, is sufficiently high.

II. Experimental Procedures

1. Specimen

The TiN specimens used in the present study were prepared by nitriding pure Ti plates, having dimensions

of $15 \times 8 \times 0.2$ (mm), at 1500 K for 504 ks (140 h) in a flow of purified nitrogen at atmospheric pressure. The Ti plate had the following impurities; Fe: <0.25 , O: <0.2 , N: <0.05 , and H: <0.013 in mass per cent.

A few specimen plates were hung with thin Pt wires from a stainless steel net during the nitridation in a reaction tube. The possible oxidation by impurity oxygen was minimized by placing piles of spongy Ti before and after the specimens in a reaction tube. After the nitridation the specimen thickness was about 0.22 mm.

X-ray diffractometry (XRD) with Cu- K_α radiation showed that the nitride is $\delta\text{-TiN}$. The exact composition of the nitride was determined by gas analysis and lattice parameter measurement to be $\text{Ti}_{0.74}\text{N}$, but it is expressed as TiN for convenience and no factors related to its composition will be dealt with in this study. The nature and oxidation behavior of the $\text{Ti}_{0.74}\text{N}$ coupon formed by the above process were reported elsewhere⁽⁴⁾.

2. Deposition of Al_2O_3 films

An apparatus similar to that used by Park *et al.*⁽⁵⁾ was used for the deposition of Al_2O_3 films. A single specimen was hung in a vertical reaction tube of transparent quartz so that it can be heated by an infra-red ray image furnace without heating the tube wall so high. When the specimen was heated in a hydrogen atmosphere to 1173 K, i.e. deposition temperature, 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 of Al_2O_3 . The AlCl_3 gas was produced by passing an HCl gas through a pile of Al chips heated to 523 K.

The conditions for the deposition were chosen as below, because they were reported⁽⁶⁾ to give the highest deposition efficiency; total gas flow rate measured at atmospheric pressure: $33 \times 10^{-6} \text{ m}^3 \cdot \text{s}^{-1}$, molar fraction of AlCl_3 : 0.01, the flow rate of H_2 is equal to that of CO_2 and is $16.3 \times 10^{-6} \text{ m}^3 \cdot \text{s}^{-1}$.

* Presented at the Annual Spring Meeting of the Japan Inst. Metals, Yokohama (1989).

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

*** Graduate Student, Osaka University. Present address: Mitsubishi Electric Corp., Himeji, Hyogo 670, Japan.

The total pressure in the reaction tube was maintained at about 50 kPa by adjusting a needle valve and operating a vacuum pump. After a specified deposition time the furnace was switched off and the specimen was cooled in a hydrogen atmosphere.

3. Oxidation tests

Isothermal oxidation tests were carried out in an oxygen flow at atmospheric pressure using an auto-recording thermobalance. The oxidation temperature ranged from 1073 to 1273 K. When a specimen was heated to a test temperature, the atmosphere was changed from argon to oxygen. The both gases were purified by passing through silica gel, phosphorous pentoxide, and alkali asbestos. After a specified period of oxidation the specimen was cooled in the argon atmosphere.

The specimens for XRD and metallographic examinations were similarly oxidized at specified temperatures for specified periods.

4. Characterization of the specimens

XRD, scanning electron microscopy (SEM), and energy dispersive X-ray microanalysis (EDX) were used for characterizing the specimens before and after the oxidation.

III. Results

1. Nature of the CVD Al_2O_3 film

Figure 1(a) and (b) show an outer surface and a fractured edge respectively of a TiN specimen coated with the

Fig. 1 Outer surfaces (a, c) and fractured edges (b, d) of the TiN specimens coated with the CVD Al_2O_3 films deposited at 1173 K for (a, b) 3.6 ks and for (c, d) 4.8 ks. The films have almost uniform thicknesses and good contact with the substrates (b, d).

Fig. 2 X-ray diffractometer charts for (a) the TiN specimen coated with the CVD Al_2O_3 film by the deposition at 1173 K for 3.6 ks, and for the coated specimens oxidized (b) at 1173 K for 97.3 ks, and (c) at 1273 K for 28.8 ks. Peaks of TiN is for δ -TiN and those for TiO_2 correspond to rutile.

Al₂O₃ film deposited at 1173 K for 3.6 ks. The substrate surface is completely covered with the film. The network structure in Fig. 1(a) seems to reflect the grain boundary of the original Ti plate developed during the nitridation. The Al₂O₃ film, at the right end in Fig. 1(b), seems dense even under SEM magnifications of up to $\times 10,000$ and to have an almost uniform thickness. The film is in complete contact with the substrate.

The films deposited at 1173 K for 1.2 and 2.4 ks showed a similar nature to those shown in Fig. 1(a) and (b) under the SEM observation, except for the film thickness.

When the deposition time was increased to 4.8 ks at the same temperature, small cracks were found mainly at the foot of the Al₂O₃ ridges forming a network structure as shown in Fig. 1(c). However, there is no observable cracks in a fractured edge of the film, Fig. 1(d). The film has again good contact with the substrate.

The result of XRD, Fig. 2(a), for the coated specimen shows peaks corresponding to δ -TiN and Al₂O₃. However, the peak for Al₂O₃ near the right end of the figure corresponds to δ -, κ -, and χ -Al₂O₃. There is a low and broad peak near 0.25π corresponding to γ -, δ -, and κ -Al₂O₃. After the oxidation at 1173 K for 97.3 ks this peak becomes slightly distinct as Fig. 2(b) shows.

The above facts indicate a possibility that the structure of the film is partly microcrystalline or amorphous. However, a further study is necessary to determine the structure exactly.

Figure 2(b) and (c) indicate that all the solid oxidation products are rutile and the structure of the film changes during the oxidation, since the peaks corresponding to Al₂O₃ vary. However, α -Al₂O₃ was not detected even after the oxidation at 1273 K for 28.8 ks, Fig. 2(c), the longest period at the highest oxidation temperature in this study. The average film thickness increased linearly with the deposition time such that; 0.78 μm for 1.2 ks, 1.6 μm for 2.4 ks, 2.6 μm for 3.6 ks, and 3.4 μm for 4.8 ks.

2. Oxidation kinetics

Figures 3 and 4 show the isothermal oxidation curves of the specimens coated with the Al₂O₃ films of about 2.6 μm thickness. Those of the uncoated specimens are also included in the figures for comparison. Here, $\Delta M \cdot A^{-1}$ represents the mass gain per unit specimen area due to oxidation.

It is seen that the Al₂O₃ films decrease the oxidation rate, however the oxidation behavior shows a breakaway after certain periods at all the temperatures tested except 1073 K. In this case no mass gain was detected for up to 185 ks.

The breakaway time, t_b , is defined here as the time where the rapid increase in the oxidation rate sets in, and is obtained from the crossing where the extrapolates of the almost linear parts of the curve before and after the breakaway meet, as shown in Fig. 4.

Figure 5 shows that t_b decreases as the oxidation temperature increases.

Figure 6 shows that t_b increases gradually with an in-

Fig. 3 Oxidation curves of the coated and uncoated specimens.

Fig. 4 Oxidation curves of the coated and uncoated specimens, and determination of t_b .

Fig. 5 Variation in t_b with the oxidation temperature.

crease in the film thickness of up to about 2 μm , beyond which it increases very rapidly. This implies that the nature of the film may change around this thickness.

3. Metallography and microanalysis

Figure 7(a) and (b) show an outer surface and a fractured edge respectively of the specimen oxidized at 1073 K for 185 ks. Though the kinetics result, Fig. 4, shows no

Fig. 6 Variation in t_b with the thickness of the CVD Al_2O_3 film.

measurable mass gain due to the oxidation, very small particles of rutile, white particles in Fig. 7(a), are formed.

There is no oxide formed beneath the film, however many small pores have developed in the substrate near the film/substrate interface.

Figure 8(a) to (c) show outer surfaces of the specimen oxidized at 1173 K for 20 ks which is shorter than t_b . There are a few small islands of oxide on the film. The results of XRD and EDX indicated that these oxides are rutile. A higher magnification view of one oxide island, Fig. 8(b), indicates that it is an aggregate of small particles loosely packed and hence it cannot be protective. Figure 8(c) shows very small rutile crystals, white particles in the center, growing on an area which looked very sound in Fig. 8(a).

Figure 8(d) shows a fractured edge of the same specimen. There is a hemispherical region occupied by very porous massive oxide under the film.

Figure 9(a) to (d) show similar features as those in Fig.

8, of the specimen oxidized at 1173 K for 40 ks which is just after t_b as confirmed by the thermogravimetry.

The size and number of the rutile aggregates growing on the film increased, Fig. 9(a). A higher magnification view, Fig. 9(b), of an aggregate shows that it is still loose. Moreover, the rutile grew on the both sides of the film as Fig. 9(c) and (d) show. This was confirmed by XRD, SEM, and EDX.

Figure 9(d) shows an example of the line analysis across the film. This figure also indicates that the film remained almost undamaged during the oxidation.

The detailed SEM observations of the specimens oxidized for various periods indicated that the growth of rutile aggregates on the film and the development of porous massive rutile under the film start at nearly the same time except for the oxidation at 1073 K, and they are localized except for very later stages of the oxidation.

There was no particular difference in the structure of the above two before and after t_b . The main difference recognized is that the growth rate of massive rutile under the film becomes larger after t_b .

IV. Discussion

1. Influence of oxidation temperature

The protectiveness of the CVD Al_2O_3 films formed in this study is satisfactory at 1073 K for at least up to 185 ks as shown by the results of kinetics, Fig. 4, and metallographic examinations, Fig. 7. The formation of small rutile particles on the film indicates that titanium moves outward through the film to form them. The transport of titanium is thought to be via solid state diffusion, because the films look very dense under the SEM observation.

On the other hand, the nitrogen liberated by the

Fig. 7 SEM micrographs of the coated specimen oxidized at 1073 K for 185 ks, showing (a) outer surface and (b) fractured edge. Small white particles in (a) are rutile.

Fig. 8 SEM micrographs of the coated specimen oxidized at 1173 K for 20 ks. (a) Outer surface showing a few rutile aggregates. (b) A higher magnification of an aggregate in (a). (c) Rutile crystals (center) growing on the film which looks very sound in (a). (d) Fractured edge showing formation of porous massive rutile at a limited area under the film.

transport of titanium seems responsible for the formation of small voids at the film/substrate interface, because there is no void of this kind before the oxidation, Fig. 1(b) and (d). Further, these voids may be occupied by gaseous nitrogen and/or nitrogen oxide.

As the oxidation temperature increases the degree of protection decreases. This is understood by the comparison of the oxidation curves between the coated and uncoated specimens in Fig. 3, and by the value of t_b which decreases as the temperature increases, Fig. 5. Particularly, at 1273 K the both curves have similar shapes except for the periods before t_b .

The growth of rutile on the both sides of the film means the inward diffusion of oxygen and outward diffusion of titanium through the film. The both were enhanced

by the temperature rise.

Even during the periods before t_b the oxidation rate is considerably higher than that of other alloys which form $\alpha\text{-Al}_2\text{O}_3$ scales as a rate limiting layer. For instance, $\Delta M \cdot A^{-1}$ is $1.2 \text{ g} \cdot \text{m}^{-2}$ for an Fe-10 mass % Al alloy oxidized at 1300 K for 50 ks⁽⁷⁾. This value is much smaller than those shown in Fig. 3.

This difference is attributable to the structure of the film. As far as the XRD indicates the film is not $\alpha\text{-Al}_2\text{O}_3$ and some structural changes take place during the oxidation. Some structural changes can induce lattice defects in the film until a stable structure is attained.

The above view is supported by the study⁽³⁾ in which $\alpha\text{-Al}_2\text{O}_3$ film formed by a CVD process provided good protection against oxidation even at 1273 K.

Fig. 9 SEM micrographs of the coated specimen oxidized at 1173 K for 40 ks. (a) Outer surface showing a few rutile aggregates. (b) A higher magnification of an aggregate in (a). (c) Fractured edge, showing the rutile aggregates on the film and porous massive rutile under it. (d) Line analysis across the film.

However, it is necessary to carry out a further study to follow the structural change of the film during the oxidation.

2. Breakaway oxidation

The reason for the breakaway observed is discussed below. The metallographic examinations showed no clear structural differences before and after t_b in the oxides formed on and under the film. However, the growth rate of the oxide under the film becomes much faster than that of the oxide aggregate on the film after t_b . From this observation it can be said that the main part of the mass gain after the breakaway corresponds to the growth of porous massive rutile under the film.

One possible explanation for the breakaway is that

nitrogen liberated by the consumption of titanium can form gaseous reaction products which can mechanically stress the film when their pressure becomes sufficiently high. The stress thus developed can cause some kind of mechanical defects in the film which would enhance the transport of oxygen into the substrate. If the mechanical defects are relatively large, gaseous transport of oxygen becomes possible, which further enhance the oxidation.

An additional reason for the breakaway is the solution of nitrogen in the film, which can increase the lattice defects to enhance the transport of oxygen through it.

The enhanced transport of oxygen again enhances the liberation of nitrogen and this cycle repeats leading to the breakaway observed.

The main point in the above explanation is based on

the structural changes which would take place during the oxidation. Therefore, it is again necessary to confirm the structural changes by a further study using instruments such as transmission electron microscope to detect lattice defects and microcracks.

V. Conclusions

(1) The CVD Al₂O₃ film formed in the present study is satisfactorily protective at 1073 K for at least up to 185 ks.

(2) The oxidation kinetics shows breakaway at temperatures between 1123 K and 1273 K.

(3) The breakaway time increases as the film thickness increases, however it decreases as the oxidation temperature rises.

(4) During the oxidation a small number of rutile aggregates grow on the film, while porous massive rutile grows under the film.

(5) The mass gain after the breakaway almost cor-

responds to the growth of porous massive rutile under the film.

Acknowledgment

The authors are grateful to Mr. J. Nakata of our laboratory for his partial assistance in the experimental work.

REFERENCES

- (1) S. Okamoto: Jitsumu Hyoumen Gijyutsu, **32** (1985), 130.
 - (2) S. Takasu and K. Shibuki: Thin Solid Films, **127** (1985), 283.
 - (3) S. Taniguchi, T. Shibata and Y. Horikawa: Boshoku Gijyutsu, **37** (1988), 745.
 - (4) S. Taniguchi, T. Shibata and A. Okada: Mater. Trans., JIM, **30** (1989), 765.
 - (5) C. S. Park, J. G. Kim and J. S. Chun: J. Vac. Sci. Technol., **1** (1983), 1820.
 - (6) R. Colmet, R. Naslain and P. Hagenmuller: J. Electrochem. Soc., **129** (1982), 1367.
 - (7) S. Taniguchi, T. Shibata and H. Tsuruoka: Trans. JIM, **28** (1987), 788.
-