General paper

INFLUENCE OF NITROGEN GAS ON THE HIGH-TEMPERATURE OXIDATION CHARACTERISTICS OF Ti-14Al-21Nb (MASS%)

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Abstract: The oxidation characteristics of Ti-14Al-21Nb has been studied with an emphasis on the influence of nitrogen. The oxidation curve in N_2 -21% O_2 is significantly lower than in O_2 or in Ar-21% O_2 at 1300 K. At the scale / substrate interface, two thin continuous layers and an Al-enriched layer were formed. These three layers were identified as /TiN/Nb₂Al/TiAl/ by XRD, EPMA, SEM, and optical observation. The oxidation rate is reduced by the formation of the TiN layer, although the oxidation of bulk material of TiN is as fast as Ti Alloy. This difference can be explained by such a low oxygen partial pressure at the interface that the TiN layer is kept intact.

Key words: Ti-14Al-21Nb, Ti₃Al, Oxidation, Nitrogen, TiN, Pressure dependency

1 INTRODUCTION

Ti-14Al-21Nb(Ti₃Al-Nb) is attractive material for airplane engines for its high specific strength at elevated temperatures. A few investigations have been made on high-temperature oxidation characteristics of this alloy[1-3], but the influence of nitrogen on its oxidation characteristics is not so well known. We found that its oxidation curve in air is lower than in purified O_2 , and it was explained by the formation of a TiN layer at the scale/substrate interface. The aim of the present study is to demonstrate the influence of nitrogen on its oxidation characteristics in detail.

2 EXPERIMENTAL DETAILS

A button ingot of Ti-14Al-21Nb alloy was prepared by argon arc melting. The ingot was 50 mm in diameter and 13 mm in thickness. After annealing of the ingot in argon at 1300 K for 600 ks, platelet specimens measuring 10×5×1 mm were cut out of it by spark machining. They were abraded with a series of SiC polishing paper of up to #1200. They were further polished to a mirror finish on a polishing cloth impregnated with alumina powders of 0.3 μ m in size and then ultrasonically washed in acetone.

Thermogravimetry was used for following the mass gain during oxidation continuously using a thermobalance with the sensitivity of 5 μ g.

Oxidation was performed with a horizontal electric furnace. The specimens, set in an alumina boat, were placed in a reaction tube, and its atmosphere was purged with oxidant gas by using a rotary pump. Then, the specimens were heated up to an oxidation temperature at a rate of 0.3 K · s⁻¹. Test was carried out in flowing oxidant gas.

The isothermal oxidation temperature ranged from 1100 K to 1300 K, but we mainly describe the oxidation characteristics at 1300 K in this paper, because we already described its oxidation characteristics at

or below 1200 K in other papers[4,5]. The oxidant gases were three kinds as follows; commercially purified oxygen (99.8 %), N_2 -21% O_2 (N_2 - O_2), Ar-21% O_2 (Ar- O_2). We used N_2 - O_2 gas because air consists mainly of N_2 and O_2 , and to avoid the influence of H_2O or CO_2 which would be present in air. These oxidant gases were induced to silica gel, P_2O_5 and alkali-asbestos to reduce H_2O and CO_2 .

The oxidized specimens were examined with X-ray diffractometry (XRD) using Cu-K α radiation at 40 kV and 30 mA. Their cross sections were examined with scanning electron microscopy (SEM) and electron probe micro analysis (EPMA).

3 RESULTS

3.1 Kinetics

The kinetic results are summarized in Figs.1 and 2. Here, Y-axis shows the mass gain per area of the specimen and X-axis shows the oxidation time. Here, t=0 means the time when the temperature of the specimen has reached the oxidation temperature.

At 1200 K, the oxidation rates are close in Ar- O_2 and in N_2 - O_2 , and the oxidation curve in O_2 is much higher than that in N_2 - O_2 and in Ar- O_2 . This difference may be because the initially formed Al_2O_3 in O_2 does not have effective continuity [4] as a barrier against oxygen diffusion. Similar results were obtained at 1100 K.

At 1300 K, the oxidation curve in Ar- O_2 becomes close to that in O_2 . This may be because the initially formed Al_2O_3 in Ar- O_2 loses the continuity at 1300 K. On the other hand, the oxidation curve in N_2 - O_2 is still lower than that in O_2 and in Ar- O_2 .

The oxidation curves at 1300 K in Ar- O_2 or in O_2 show temporal acceleration. As we already reported [5], this acceleration is caused by local destruction and healing of the scale. In N_2 - O_2 , the oxidation curve is nearly parabolic even at 1300 K.

Generally, the oxidation mass gain as a function of

Fig.1. Oxidation curves at 1200 K.

Fig.2. Oxidation curves at 1300 K.

Fig.3. Reciprocal of reaction order at 1200 K.

Fig.4. Reciprocal of reaction order at 1300 K.

oxidation time can be expressed as Eq. (1).

$$Y^n = K \cdot t. \quad (1)$$

Y : mass gain per area of specimen

n : reaction order

K : reaction rate constant

(when $n=2$, K is parabolic rate constant K_p)

t : oxidation time

Equation (2) is obtained by taking logarithm of Eq. (1).

$$\ln(Y) = A \cdot \ln(t) + B. \quad (2)$$

A : $1/n$

B : $\ln(K)/n$

Equation (2) means that the reciprocal of instantaneous reaction order, $1/n$, can be obtained from derivative of logarithm of mass gain with respect to logarithm of oxidation time. Figures 3 and 4 are plots of $1/n$ value vs. oxidation time. When the oxidation follows a parabolic law, $1/n$ is 0.5. Generally, this value ranged from 0.4 to 0.6, nearly equal to 0.5, but, sometimes up to almost 1 in O_2 and in $Ar-O_2$ at 1300 K. This means the temporal transition to a linear law.

3.2 Metallography and Analyses

The metallographic and analytical results of the specimens oxidized at 1200 K were already shown in another paper in detail[4]. So, we will describe mainly about the results of 1300 K oxidation here.

Figures 5 to 7 are SEM micrographs and EPMA (EDS and WDS) elemental maps of cross sections of the specimen oxidized at 1300 K for 100 ks.

The scales in Figs.5 to 7 have common structure as below. They consist of three layers. The outermost layer A is almost TiO_2 . This TiO_2 layer is densified and the grain is coarsened by sintering. Percentage of Ti to all metallic elements in this layer, which is measured by the semi-quantitative EDS, is more than 90 mol%. Beneath this TiO_2 layer, Al_2O_3 grains, which may be formed in early period of oxidation, is concentrated in B. Percentage of Al to all metallic elements in this Al_2O_3 grains is more than 98 mol%.

Fig.5. SEM image and elemental maps of a cross section of the specimen oxidized in O_2 for 100 ks at 1300 K.

Fig.6. SEM image and elemental maps of a cross section of the specimen oxidized in N_2-O_2 for 100 ks at 1300 K.

Fig.7. SEM image and elemental maps of a cross section of the specimen oxidized in $Ar-O_2$ for 100 ks at 1300 K.

Fig.8. More detailed observation of layered structure at scalesubstrate interface of the specimen oxidized in N_2-O_2 for 100 ks at 1300 K.

Fig.9. Results of WDS linear analysis.

Fig.10. Results of X-Ray Diffraction.

This Al_2O_3 concentrated layer is not continuous. So, the oxidation resistance of this scale is not good. The innermost layer C is the mixture of TiO_2 and Al_2O_3 fine grains. This layer may be formed by inward diffusion of oxygen, because the metallic composition of this layer nearly equal to that of the substrate except for the graduation of niobium concentration caused by selective oxidation of Ti and Al.

In the oxidation in $\text{N}_2\text{-O}_2$, layers D (TiN), E (Nb_2Al) and F (TiAl) were formed beneath layer C. These layers D, E and F can be seen only in the specimen oxidized in $\text{N}_2\text{-O}_2$. The identification of these layers will be described later. The formation of these layers is caused by selective nitridation of Ti. The detailed observation is shown in Fig.8. Figure 9 is the results of WDS line analysis. Nb is concentrated beneath the TiN layer. As going across the Nb concentrated layer, which may be Nb_2Al , N is decreasing to the noise level.

Figure 10 is the results of XRD which was performed at several positions from surface to substrate. The top line was obtained at the scale surface. Then, the scale was detached by mechanical stress. The second line was obtained at this spalled face. The rest three lines were the results of the series of polishing and measurement.

According to these XRD results, the peaks of TiO_2 are becoming lower toward the substrate. Contrarily, the peak intensities of TiN and Nb_2Al are becoming higher. In the polishing, there was a golden brownish layer, which looks like the color of TiN. The schematic drawing for the scale structure based on these results is shown in Fig.11.

4 DISCUSSION

As mentioned above, the oxidation of Ti-14Al-21Nb in $\text{N}_2\text{-O}_2$ causes the formation of TiN and the reduction of the oxidation rate.

Al is enriched beneath the Nb_2Al layer and forms a $\gamma\text{-TiAl}$ which has lower oxygen solubility than $\alpha_2\text{-Ti}_3\text{Al}$ [6,7] can disturb the formation of an oxygen-dissolved layer which is seen in the specimens oxidized in O_2 or in Ar-O_2 . However, from the result of WDS, oxygen flux may be stopped at the

A:Rutile

B:Alumina concentrated

C:mixture of fine grained oxide

D:TiN
E: Nb_2Al
F:TiAl

Substrate
(Ti-14Al-21Nb)

Fig.11. Schematic drawing of the scale.

TiN layer. So, it perplex whether the disturbance of the formation of the oxygen-dissolved layer caused by TiAl or TiN.

The nitride was identified as TiN by XRD, EPMA (EDS and WDS), SEM, and optical observation. This result agrees with the result of Wallace et al.[8]. Thermodynamic possibility of selective nitridation will be discussed in another paper [4].

From the WDS result (Fig.9), the oxygen concentration dropped to the noise level beneath the TiN layer. So TiN seems to act as the barrier against the inward flux of oxygen. However, the oxidation rate of a TiN platelet or TiN composite is much larger than that of Ti-14Al-21Nb [9,10].

The oxidation rate of TiN platelet has two stages: initially parabolic stage and secondary (pseudo)linear stage. In (pseudo)linear stage, oxidation rate has dependence on the oxygen partial pressure. According to Desmaison et al.[10,11] the dependency of parabolic rate constant K_P ($\text{kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}$) on oxygen partial pressure P (Pa) can be assumed by Eq.(3).

$$P = 133.3 \times \frac{K_P}{12.96 \times 10^{-9} - 3.71 \times 10^{-2} \times K_P} \quad (3)$$

The parabolic rate constant of Ti-14Al-21Nb is $15 \times 10^{-9} \text{ (kg}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}\text{)}$ in $\text{N}_2\text{-O}_2$ at 1300 K. The oxygen partial pressure, calculated from Eq.(3) and this value of K_P , is 161(Pa). So if the oxygen partial pressure at the scale / TiN interface is lower than this value, TiN can not be easily oxidized, and does perform as a protective layer.

To explain this hypothesis, we demonstrated the experiment at 1300 K as shown below.

At first, the specimen was oxidized in $\text{N}_2\text{-O}_2$ for 100 ks to form a TiN layer beneath the scale. Then, the experimental atmosphere was purged with purified O_2 , so the supply of nitrogen is terminated at 100 ks. Then, the furnace was cooled down to room temperature. By this cooling, the scale was cracked by thermal stress, and the oxygen partial pressure at the scale / TiN interface must be increased up to nearly atmospheric pressure by gaseous diffusion through crack.

The specimen was reheated to continue the oxidation test. In order to separate the influence of the termination of the nitrogen supply, that oxidation test without cooling (without cracking) and continuous oxidation in N_2-O_2 was also performed.

The results of this experiment are shown in Fig.12. The oxidation curve of TiN in O_2 and that of Ti-14Al-21Nb in O_2 are also shown in Fig.12. If the specimen was cooled, namely the scale was cracked, oxidation curve shows drastic increase. In contrast to this, if the specimen was oxidized without cooling after purging to purified O_2 , namely without cracking of the scale, the oxidation curve obeys a parabolic law with slight shift to a linear law. If the specimen was continuously oxidized in N_2-O_2 , the oxidation curve obeys a parabolic law with slight shift to a cubic law.

From these results, we can conclude that the oxidation rate of TiN has a strong dependency on oxygen partial pressure at the scale / TiN interface, and TiN shows oxidation resistance only under a low oxygen pressure.

The slight shift from parabolic to linear law observed with the specimen without crack may be caused by moderate oxidation of TiN. The evidence of the moderate oxidation can be seen in Fig.13. The shift to cubic law observed with the specimen which was continuously oxidized in N_2-O_2 may be caused by the change of protectivity of the scale, such as the growth of TiN.

Figure 13 is cross sectional SEM micrographs at the scale / substrate interface of the specimen oxidized for totally 500 ks (for 100 ks in N_2-O_2 and for 400 ks in O_2) without cracking. Elemental maps of O, Ti, and

Fig.12. Oxidation curves at 1300 K, showing the influence of gaseous pressure.

N show that TiN layer D' is moderately oxidized and nitrogen is migrated. From Nb map and SEM image, it can be said that Nb_2Al , layer E, still exists at the scale/metal interface. The TiAl layer disappears, and Al is concentrated at the inner part G of scale.

Fig.13. SEM image and elemental maps. Oxidized for 400 ks in O_2 after preoxidation in N_2-O_2 for 100 ks and without cooling.

5 CONCLUSIONS

The influence of nitrogen on high-temperature oxidation of Ti-14Al-21Nb has been investigated mainly at 1300 K. The main results obtained are shown below.

1. Oxidation rate in N_2-O_2 is undeniably lower than that in O_2 and $Ar-O_2$. This reduction of oxidation rate is caused by the formation of a TiN layer.
2. TiN shows oxidation resistance only under a low oxygen pressure such as beneath the scale. This can be explained by oxygen partial pressure dependency of parabolic rate constant of TiN.
3. When the supply of nitrogen is stopped and the oxidation of the specimen is continued in pure O_2 , the TiN layer is oxidized moderately and the oxidation curve approaches to linear law from parabolic law.

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