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ABSTRACT
Burn resistant titanium alloys have been investigated; however burn resistant mechanism and burning behavior of titanium alloys were not clear. The fast bum C.P.Ti and Ti-6-4 alloy were compared with the Ti40 alloy. The burning velocity of C.P.Ti, Ti-6-4 and Ti40 are 1.27 mg/s, 1.54 mg/s and 0.1 mg/s, respectively. TiO2 is the major burning products after C.P.Ti burns. Mixture oxides of Ti, V and Al form after Ti-6-4 burn. Mixture oxides of Ti and V form after Ti40 burnt. These oxides are porous and have cracks. Rich Cr layer emerges at the interface between burning products and matrix for Ti40 alloy. The Cr-rich layer is in the form of Cr2O3, which is closely woven products and tenacity. This layer can retard oxygen diffusion into the matrix and prevent burning chemical reactions. Ti-40 alloy reveals good burn resistant properties. Burn-resistant mechanisms of fast scatter dispersion of heat and suspending oxygen transfers are put forward.

Key words: burn resistant titanium alloys, burn resistant mechanism, evaluation method of burn resistant Behavior, physical properties, burning behavior.

1. INTRODUCTS
Titanium and its alloys possess good comprehensive properties and are widely used in many industrial fields. However “Titanium fire" took place for several times in the aircraft engines. In order to avoid the titanium fire and meet the requirement of advanced aircraft engines and rivets, several burn resistant titanium alloys have been investigated, for example, Alloy C(Ti-35V-15Cr)[1-2], Ti-45Nb[3], BTT-1/BTT-3(Ti-Al-Cu)[4], Ti40(Ti-25V-15Cr-Si)[5] and Ti14(Ti-13Cu-1Al-Si)[5]. Their mechanical properties have been reported. Although there were burn resistant titanium alloys and different evaluational methods for non-burning behavior (such as laser ignition method[6], high speed frictional method[7], and fracture method[8]), burn resistant mechanism was not clear. The goals of the present paper are to study the burning characteristic of conventional titanium alloys and analyze the burn resistant mechanism of Ti40 alloy. The evaluational methods for burning behavior were metal liquid drop method and DCSB method[9].

2. EXPERIMENTAL PROCEDURES
Ti-40 alloy used in this paper was prepared through vacuum suspense furnace melting for four times, then forged and rolled to sheet of 2mm in thickness. Other comparative titanium alloys, such as C.P.Ti, TC4(Ti-6Al-V) and TB3(Ti-3Al-8V-10Mo-2Fe) were 2mm mill sheet in thickness. Metal liquid drop (MLD) method and DCSB method were used to examine their burning behavior. MLD method was used to spurt the melted liquid drop of C.P.Ti to the specimen surface with high pressure. The liquid drop could cause the specimen to burn and the burning area was examined. DCSB method was used to ignite the specimen for some time at certain current and voltage, and the burned weight was examined. SEM, EDAX and X-ray diffractomater were used to examine their burned microstructures and products.

3. RESULTS

3.1. BURNING BEHAVIOR
The burning behavior of several titanium alloys is shown in Fig.1. Both MLD and DCSB methods have the same effect. C.P.Ti and Ti-6-4 are burnt fast, and their burning velocity in DCSB is 1.27 mg/s and 1.54 mg/s respectively. Ti40 alloy reveals good burn resistant behavior, and its burning velocity in DCSB is 0.1 mg/s. Their burning area in MLD is 28%, 14% and 0 respectively.

3.2 MICROSTRUCTURES AFTER BURNING
Fig. 1. Burning behavior of several titanium alloys
a) MLD  b) DCSB

The product surfaces after C.P.Ti, Ti-6-4 and Ti40 burnt are illustrated in Fig.2. Fig.3 is their interface images between burnt products and matrix. Micro-cracks appear on their product surface, their surface oxide layers are porous (the reasons see reference [9]), and the interface oxide layers and product internal oxide layers (Fig.4) of C.P.Ti and Ti-6-4 alloy are also porous, which can not prevent oxygen from diffusing into matrix. TiO$_2$ is

Fig. 2. Product surface images after titanium alloys burnt
a) C.P.Ti  b) Ti-6-4  c) Ti40

Fig. 3. Interface images between burnt products and matrix
a) C.P.Ti  b) Ti-6-4  c) Ti40
the major burnt products burnt for C.P.Ti, as shown in Fig.5. Mixture oxides of Ti, V and Al form after Ti-6-4 burn (Fig.5). Mixture oxides of Ti and V form after Ti40 burn. However the interface of Ti40 alloy does not emerge cracks, and its oxide layer is comparatively tenacious. Fig.6 shows the EDAX of burnt product surface and interface of Ti-6-4 and Ti40 alloys. The differences of chemical compositions for Ti-6-4 between surface and interface are very small. Alloying elemental Cr for Ti40 alloy does not appear on the surface. However lots of Cr are enriched on its interface, existing in the form of Cr2O3, which retards the diffusion of oxygen.

4. DISCUSSION

4.1 FACTORS INFLUENCING BURN RESISTANT BEHAVIOR

The burn resistant behavior is determined the melting point, thermal conductivity, heat of oxidation, structure, oxide layer and so on

a) Oxide film

Just as above mentioned, product surface of C.P.Ti, Ti-6-4 and Ti40 alloys is porous, and can not prevent oxygen from transforming to matrix. But interfacial oxide layer of Ti40 alloy is tenacious, and can effectively retard oxygen diffusion into the matrix, and prevent from continuous burning.

b) Melting point

Table 1 lists melting point of several titanium alloys. Ti-V-Cr alloy has a lower melting point. Ti-alloys with low melting point will soften or melt before burn, and lots of heat is absorbed, thereby the local temperature decreases
and the burning is avoided. On the other hand, the Ti-alloy parts with low melting point will soften before burning, so that rigid friction is also avoided (rigid friction is the major reason for titanium fire in aircraft engines), preventing titanium parts from burning.

Table 1 Melting point of several titanium alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>C.P.Ti</th>
<th>TC4</th>
<th>Ti6242</th>
<th>βc</th>
<th>Ti-V-Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>melting point(°C)</td>
<td>1668</td>
<td>1650</td>
<td>1700</td>
<td>1650</td>
<td>1580</td>
</tr>
</tbody>
</table>

c) Thermal conductivity

Table 2 demonstrates the thermal conductivity of several titanium alloys. The thermal conductivity of Ti-V-Cr alloy is about 10 times bigger than that of conventional titanium alloys. Its burn factor\[^{13}\] (defined as the ratio of heat of oxidation to thermal conductivity) reduces obviously. Alloys with high thermal conductivity can decrease burn possibility because high thermal conductivity is beneficial for heat transform and heat uniform distribution, which prevents local temperature increasing and leads to decrease of burn danger.

Table 2 Thermal conductivity of several titanium alloys(cal/s. °C)

<table>
<thead>
<tr>
<th>Alloys</th>
<th>25°C</th>
<th>100°C</th>
<th>200°C</th>
<th>300°C</th>
<th>400°C</th>
<th>500°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.P.Ti</td>
<td>0.039</td>
<td>0.039</td>
<td>0.039</td>
<td>0.040</td>
<td>0.041</td>
<td>0.043</td>
</tr>
<tr>
<td>Ti-6-4</td>
<td>0.013</td>
<td>0.016</td>
<td>0.021</td>
<td>0.025</td>
<td>0.030</td>
<td>0.034</td>
</tr>
<tr>
<td>Ti-V-Cr</td>
<td>0.223</td>
<td>0.247</td>
<td>0.292</td>
<td>0.341</td>
<td>0.394</td>
<td>0.420</td>
</tr>
</tbody>
</table>

d) Heat of oxidation

Oxidation activation energy of Ti-25V-15Cr alloy is 399KJ/mol at 700°C\[^{14}\]. At the same temperature, the oxidation activation energy of Ti-6-4 and IMI834 is 267KJ/mol\[^{13}\]. The higher activation energy, the more difficult to oxide. Open oxidation a tenacious and protective oxide film forms on the alloy’s surface, which retards oxygen diffusion into the matrix. High activation energy indicates low heat of oxidation, which decreases burning factor and increases burning resistant behavior.

d) structures

Ti-40 alloy is a stable single β phase alloy\[^{10}\]. Single β phase structure is important for burning resistant behavior\[^{3}\], because expansion of prior α grains on the thermally-induced α/β transformations disrupts any formed ignition inhibiting oxide layer. Cracks in the oxide layer over α grains will serve as a diffusion path for oxygen; the oxide layer over β grains will remain intact on heating from an incipient ignition site, and continue to provide ignition resistance.
4.2 MATHEMATICAL MODEL FOR BURN RESISTANCE

As above analysis, titanium alloy's melting point(Tm), thermal conductivity(λ), heat of oxidation(Q), oxide layer (e) and structures(m) influence their burn resistant behavior.

If burn resistant capacity 1/K is expressed by non-burning temperature, 1/K can be given as follows:

\[ 1/K = f(Tm, \lambda, Q, m, e) \]  \hspace{1em} (1)

If burning factor \((Q/\lambda)\) is used, \(m\) and \(e\) is assumed as a coefficient \(n\), formulation (1) can be transformed to:

\[ 1/K = n \cdot f(Tm, Q/\lambda) \]  \hspace{1em} (2)

for \(Q/\lambda\) item, we should consider else specific heat (c), expansion coefficient (α), specimen size (p) and experimental conditions (i.e. imputing energy q , and time t) for the same dimension, therefore:

\[ 1/K = n \cdot [Tm + Q \cdot c/(\lambda \cdot \alpha \cdot t \cdot p \cdot q)] \]  \hspace{1em} (3)

The higher of expansion coefficient and thermal conductivity and lower heat of oxidation, melting point and specific heat, the higher the K and the better the burn resistant behavior, as shown in formulation (3).

Table 3  Expansion coefficient α of several titanium alloys (0 – 100°C, \(\times 10^6/°C\))

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C.P.Ti</th>
<th>TA6</th>
<th>TB2</th>
<th>TC4</th>
<th>TC9</th>
<th>Ti-V-Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>8.0</td>
<td>8.3</td>
<td>8.53</td>
<td>8.53</td>
<td>7.7</td>
<td>9.17</td>
</tr>
</tbody>
</table>

Compared with the conventional titanium alloys, the Ti-V-Cr alloy exhibiting has lower melting point, lower heat of oxidation, higher thermal conductivity, and higher expansion coefficient (as shown in Table 3) and reveals a good burn resistant behavior. On the other hand, experimental conditions and the specimen size also influence the burning resistant properties, as shown in eqn.(3). These results can be verified by two evaluation methods, i.e MLD and DCSB.

4.3 BURN RESISTANT MECHANISMS

4.3.1 Four necessary factors of burning

We can not separate the burning of titanium and its alloys from oxygen, heat, burning materials and chemical reactions. These four factors are independent, and every one is necessary. Fig.7 is the three-dimensional profile of titanium burning. If any one is retarded among these four factors, the burning stops.

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Oxygen:
The cohesion of titanium with oxygen is high. The burning of titanium is preserved by oxygen from air. Without oxygen titanium is impossible to burn. But no oxygen is impossible.

Heat:
There were many ways to provide the necessary heat to ignite metals, for example, laser ignition method, frictional method, DCSB etc.. If the source of heat is removed away the burning is avoided. If so, titanium alloys can not be used in aviation engines.

Burning materials:
The burning materials here are titanium alloys. Their surface area is one of important factors for ignition. The bigger of the surface area, the easier for ignition. Their thermal conductivity is another important factor.

Chemical reactions:
Chemical reactions are the serious oxygen reactions between alloying elements, including titanium matrix, and oxygen:

\[ 2xM + yO_2 = 2M_xO_y \]
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Fig. 7 Three-dimensional profile of titanium burning
and, the interaction among oxides. These reactions are almost giving out ones, which increases the burning heat, and accelerates the burn.

4.3.2 Burn resistant mechanisms

a) Mechanism of fast scatter dispersion of heat:
If the heat of ignition titanium is fast scatterly dispersing, the local temperature decreased, preventing the metal from burning, just as shown in equation (3).

b) Mechanism of suspending oxygen transfer
An important condition of continuously burning for titanium alloys is the continuous transferring of oxygen from air to the matrix through the porous oxide layer with cracks. If some oxides retard the transferring of oxygen to the matrix for certain reasons, it can stop burning. If the tenacious and protective oxide film (as shown in fig.3) were formed when Ti40 alloy burns, it can suspend the transferring of oxygen to matrix, and retard the burning.

5. CONCLUSIONS

1) MLD and DCSB methods are used for studying burn resistant behavior. C.P.Ti and Ti-6-4 are fast to burn. Ti-40 alloy reveals good burn resistant behavior due to its low melting point, high thermal conductivity, low oxidation heat and the stable single β phase structure.
2) A mathematical model for burn resistance is given: \( I/K = n [Tm + Qc/(\lambda + \rho)] \). Taken advantage of this model, the effects of materials physical properties, experimental conditions and sample size on burn resistant behavior can be explained.
3) Four necessary factors of burning and non-burning mechanisms of fast scatter dispersion of heat and suspending oxygen transfer are put forward.

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