B. Oxidation and Oxidation Mechanism
OXIDATION OF TITANIUM BASE ALLOYS
FOR APPLICATION IN TURBINES

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Introduction

Due to the low densities of titanium base alloys, their use in turbo­
motors is particularly interesting, especially for the rotating pieces in
the hot parts of the engines where the benefit is due both to the low mass
and low inertia. However, two problems are limiting the use of these alloys :
the creep resistance and the oxidation resistance ; this study was devoted
to the later.

Numerous studies (1-4) have already been performed on the oxidation of
titanium and titanium alloys at high temperatures, i.e. over 700°C, due to
the easiness of the experimental procedures. It was then supposed that the
datas gathered at those temperatures could be transposed to a lower tempe­
rature range : i.e. the actual and potential working temperature range :
400 - 600°C. Some recent experiments (5) have shown that this assumption
was not fullfilled in the case of titanium alloys. Thus, it was decided to
extend toward the low temperatures the previous studies on industrial and
experimental alloys. Specific binary alloys have also been included in this
study in order to precise the effect of the different alloying elements.

Experimental Procedure

The different studied alloys are reported on the tables 1 and 2. The
oxidation tests were performed in air and oxygen between 100 torr and the
atmospheric pressure.

Moreover, previous works (3,6) having demonstrated the influence of
water vapour in the atmosphere, some experiments were conducted in moist
air. The reaction kinetics were followed up to 140 days and between 400
and 800°C either by continuous thermogravimetric measurements (thermobalan­
ces SETARAM B70 and MTR10.8 with a respective sensitivity of 50 and 0.1 µg)
or by discontinuous weighings of the samples (METTLER, 50 µg). Prior to oxi­
dation, the sample surface was mechanically polished with a 600 grit SiC
paper. After the recording of the oxidation kinetics, the oxide scales were

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Table 1 Industrial Alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>AFNOR</th>
<th>Composition wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unalloyed titanium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T35</td>
<td></td>
<td>O₂ ≤ 0.20 Fe ≤ 0.20</td>
</tr>
<tr>
<td>T60</td>
<td></td>
<td>O₂ ≤ 0.40 Fe ≤ 0.35</td>
</tr>
<tr>
<td>Binary alloys</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti Pd</td>
<td></td>
<td>T35 + 0.2 Pd</td>
</tr>
<tr>
<td>Ti Ni</td>
<td>TNI1.5</td>
<td>T35 + 1.5 Ni</td>
</tr>
<tr>
<td>Ti Cu</td>
<td>TCU2.5</td>
<td>T35 + 2.5 Cu</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al Zr V Sn Mo Si</td>
</tr>
<tr>
<td>α Alloys</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TA5E</td>
<td>TA5E</td>
<td>5</td>
</tr>
<tr>
<td>651A</td>
<td>TA625ED</td>
<td>6 5 2 1 0.25</td>
</tr>
<tr>
<td>6665</td>
<td>TA625D</td>
<td>6 5</td>
</tr>
<tr>
<td>6242</td>
<td>TA624ED</td>
<td>6 4 2 2 0.12</td>
</tr>
<tr>
<td>α + β Alloys</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TA3V</td>
<td>TA3V</td>
<td>3</td>
</tr>
<tr>
<td>TA6V</td>
<td>TA6V</td>
<td>6</td>
</tr>
<tr>
<td>662</td>
<td>TA6VE</td>
<td>6 6 2</td>
</tr>
<tr>
<td>550</td>
<td>TA4VE</td>
<td>4 2 4 0.5</td>
</tr>
<tr>
<td>β Alloys</td>
<td></td>
<td></td>
</tr>
<tr>
<td>β III</td>
<td>TD122E</td>
<td>6 4.5 11.5</td>
</tr>
</tbody>
</table>

Table 2 Experimental Alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Compositions, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti - Al</td>
<td>T35 + 1.65, 3, 6, 9 and 10 Al</td>
</tr>
<tr>
<td>Ti - Zr</td>
<td>T35 + 2, 4, 6 and 8 Zr</td>
</tr>
<tr>
<td>Ti - V</td>
<td>T35 + 2, 4, 6 and 15 V</td>
</tr>
<tr>
<td>Ti - Cu</td>
<td>T35 + 5.9 and 12 Cu</td>
</tr>
<tr>
<td>Ti - Fe</td>
<td>T35 + 0.3, 0.6 and 1 Fe</td>
</tr>
<tr>
<td>Ti - Nb</td>
<td>T35 + 20 Nb</td>
</tr>
<tr>
<td>Ti - Cr</td>
<td>T35 + 4, 11 and 19 Cr</td>
</tr>
<tr>
<td>Ti - Si</td>
<td>T35 + 0.5 and 1 Si</td>
</tr>
</tbody>
</table>

observed mainly by scanning electron microscopy and analysed by X-rays diffractometry and spectrometry.

Experimental Results

As mentioned previously, the weight gains during the oxidation runs were recorded, depending upon the duration of the experiments, either by
continuous or discontinuous weighings. In the second case, it was clear that the periodic cooling of the sample could have an effect on the oxidation process, due to the cracking of the oxide scale submitted to thermal stresses (7,8). This effect was investigated for each alloy and was the most marked for the TA6V (fig. 1).

![Graph showing oxidation durations: 168 hours for continuous and discontinuous weighings](image)

**FIGURE 1:** Effect of periodic coolings for discontinuous weighing measurements comparatively to continuous "in situ" measurements in the case of the TA6V alloy

Nevertheless, it appeared that the qualitative classification of the alloys from the point of view of their oxidation resistance was not modified by comparison to the continuous weighing method. Consequently, for the long time runs, discontinuous weighings were used to record the oxidation kinetics.

1) **Industrial alloys**

The weight gain curves recorded for the industrial alloys under the conditions above mentioned are partially reproduced on the figures 2 and 3.

From a metallurgical point of view, these alloys belong to different structures: α, super α, α + β and β. In our experimental conditions, it does not appear that the metallurgical structure plays a significant role on the oxidation process. Nevertheless, one can notice that all the α alloys have an oxidation rate very similar to that of pure titanium. From a technological point of view, among the tested alloys, the better oxidation resistance is exhibited by the alloys 685 (9,10), 6242, 651A and 550, the
FIGURE 2: Comparative oxidation kinetics for different industrial titanium alloys oxidized at 550°C in air.

FIGURE 3: Comparative oxidation kinetics for different industrial titanium alloys oxidized at 600°C in air.
three formers being of super α structure. Moreover, the thermomechanical treatments may have a noticeable influence on the oxidation resistance of these alloys; this can be illustrated for instance by the behavior of the β III alloy (fig. 4).

![Graph](https://via.placeholder.com/150)

**FIGURE 4 : Influence of the thermomechanical treatments on the oxidation kinetics of βIII oxidized at 600°C in air**

1. treated 15 min at 775°C and water quenched
2. homogenised at 850°C

From comparisons between the oxidation kinetics it can be deduced that the effect of the alloying elements on the oxidation resistance of titanium is the following:
- Al is favourable.
- Mo and Si are favourable but their respective influence cannot be easily appreciated.
- Sn does not seem to have a significant effect.
- V is unfavourable, especially as the temperature increases.

**ii) Experimental binary alloys**

In order to precise the respective influence of each alloying element, binary alloys were elaborated (table 2) by melting titanium T35 with selected additions in an electric arc furnace. The results obtained with the discontinuous weighing method for five binary systems at 550°C and for 50 days exposure are schematically represented on the figure 5. The results are qualitatively similar at 600°C. It appears clearly that the only element which has an important effect on the oxidation resistance of titanium
is the vanadium over 2 wt %. Unfortunately, this effect is unfavourable and increases with the vanadium content. For example, the kinetic curves for the Ti-V15 alloy show the catastrophic effect of vanadium at temperatures well below the melting point of V₂O₅ which could have been thought to be responsible for this behavior. In fact, two types of vanadium oxide have been detected: V₂O₃ in the early stages of the oxidation reaction and V₂O₅ (fig. 6 and 7) in the later stages.

At low temperatures (550°-600°C), the influence of aluminium is noticeable but not very important; in these conditions, its concentration has not a marked effect on the improvement of the oxidation resistance (in the range 1-10 wt %). However, when the temperature is increased, the influence of aluminium grows and its concentration plays then a more significant role. One can add that the beneficial effect of aluminium is especially prominent under isothermal conditions (fig. 8), the alumina protective barrier grown over the rutile oxide layer being very sensitive to thermal shocks.

On the contrary, in the case of Ti-Cr alloys, the influence of the concentration of the alloying element is very important (fig. 9). Unfortunately, it seems necessary to reach a very high chromium content (10 to 12 wt %) in order to observe a slight improvement of the oxidation resistance comparatively to pure titanium. Moreover, for the lower chromium contents, an exfoliation of the oxide scale occurs under thermal cycling conditions (fig. 10).
FIGURE 6: Oxidation kinetics of Ti-V15 in oxygen at different temperatures comparatively to pure titanium.

FIGURE 7: Scanning electron micrography of the surface of a Ti-V15 sample oxidized at 550°C during 120 hours in oxygen (Po2 = 100 torr). (1 : TiO2 ; 2 : V2O5)

FIGURE 8: Oxidation kinetics of Ti-Al1.65 and Ti-Al10 alloys comparatively to pure titanium at 650°C in oxygen.
The influence of silicon is much more promising. For relatively low concentrations as 0.5 wt %, the improvement of the oxidation resistance of titanium is considerable (fig. 11). The influence of the silicon content does not seem to have a marked effect and thus, it appears that a low content may be adequate to give a satisfactory effect.

Conclusion

Apart from considerations about the mechanical resistance of the studied alloys, two elements modify considerably the oxidation resistance of titanium: vanadium and silicon. The effect of the later is favourable while that of the former is very unfavourable. The other studied alloying elements have no marked effect; however, one can notice that Al and Zr have a slightly favourable effect.

As for the structure of the alloys, the experimental results could a priori suggest that it could step into the classification of the alloys versus their oxidation resistance; in fact, the structure does not seem to play a significant role if one consider the influence of the alloying elements; indeed, the "low alloyed" without Si or V behave very similarly to pure titanium independantly of their structure and the behavior of the α + β alloys depends mainly on the presence and concentration of vanadium; as to the super α alloys which behave all very similarly, they all contain silicon.
OXIDATION OF TITANIUM BASE ALLOYS

FIGURE 10: Comparative oxidation kinetics of Ti-Cr4, Ti-Cr11 and Ti-Cr19 alloys in air at 650°C (discontinuous weighings).

FIGURE 11: Oxidation kinetics of Ti-Si0.5 and Ti-Si1 alloys comparatively to pure titanium in air at 700°C.
The preparation of the samples (thermomechanical treatments, surface polishing) can influence the oxidation resistance as well as the nature of the atmosphere and the thermal conditions. Moreover, taking into account the structure of the oxide scales formed on titanium, this work suggest that, apart from the transport properties, any modification of the mechanical properties of the metal-oxide system (adherence, plasticity) will have a considerable influence on the oxidation resistance of titanium base alloys.

References