Oxidation Behavior of TiB₂/Ta-W Composites

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Abstract: TiB₂/Ta-W composites and Ta-10W alloy are prepared by hot-press sintering. The composites and alloy are oxidized in air at 700°C, 800°C and 900°C, respectively. The phase components of the as-prepared composites, alloy and oxidized layer were analyzed through XRD and SEM/EDS. The results showed that TiB₂ reacted with both tantalum and tantalum oxide on the surface of Ta particles, which leads to the formation of intermetallic compounds Ta₂B and Ta₃B₂. An oxidation layer of Ta₂O₅ solid solution was identified. Oxidation kinetics curves of all samples in air obeyed linear law, because a stable protective oxide scale could not be formed on the surface of samples.

1. Introduction

Tantalum has been considered as a potential material of aero-engine industry due to high melting point, excellent mechanical properties and fabricability. Tungsten is always used as solid strength additive for tantalum alloy due to the high strength and lower cost of Tungsten. Owing to a combination of high bending strength and wear at high temperature, the Ta-W alloys are considered as candidate materials for aero-engine industry. However, the low oxidation resistance of Ta-W at high temperature restricts its application[1-3]. To improve the oxidation resistance of Ta-W, Surface coatings of Hf-Si-Al and Ir-Si are usually used to protect alloy in atmosphere [4].Elements (such as Al, Cr and Si) addition in alloy has also been focused to form dense oxidation layer in order to improve alloy oxidation resistance [5]. However, the low melting point of the added elements will decrease the mechanical properties of Ta-W at high temperature. The boride ceramics(ZrB₂ and TiB₂) and Ta-W alloy behave similarly high melting point. Li et al [6] found that the oxidation behavior of Ti based alloy had been improved with the addition of TiB₂.

In this work, TiB₂/Ta-W composites and Ta-W alloy were prepared by hot-press sintering. The composites and alloy were oxidized in air at 700°C, 800°C and 900°C, respectively. The microstructure of the composites and oxidation behavior were investigated.

2. Experimental

The Ta (99.5% nominal purity, Dₜ₀=15μm), W (99.9% nominal purity, Dₜ₀=10μm) and TiB₂ (97.5 nominal purity, Dₜ₀=4.5μm) powders were mixed in a conventional ball milling for 12 h using ZrO balls with ball to powder ratio (BPR) of 1:1. And then, the mixed powders were transferred into a graphite die in a glove box under the argon atmosphere. Furthermore, Hot press(HP) sintering was performed for 1 h at 1950°C under 30 MPa with high purity Ar protection. The heating rate was 20 °C/min. The components of the samples are listed in Table 1.

After sintered, the density of the sample was determined by the Archimedes method. Vickers hardness was measured with a load of 4.9 N for 15 s, and ten different positions on polished surface
were tested to obtain an average value. The crystal structures were identified by XRD (Shimadzu XRD-6000), using CuKα as radiation with 2θ range of 10°-80°. To perform the oxidation behavior measurement, the specimens were cut into 10mm×10mm×4mm with polishing to mirror surface. The samples were placed in a muffle furnace at 700°C, 800°C and 900°C for testing circle oxidation behavior. The duration of oxidation was 4h, and samples were weighted every half an hour by the electronic balance. The microstructure and chemical distribution were analyzed with a scanning electron microscope (SEM-JSM-2100F), equipped with an energy-dispersive X-ray spectroscopy (EDS). An electron probe X-ray micro-analyzer (EPMA) with wavelength dispersive detectors (JXA-8200, JEOL, Japan) was used to investigate the chemistry of the interested phases.

Table 1. Component, density and Vickers hardness of samples.

| Sample code       | Sample component/Vol% | Density /g*cm⁻³ | HV/MPa |
|-------------------|-----------------------|-----------------|-------|
| TiB₂              | W                     | Ta              |
| Ta-10W alloy      | 0                     | 10 Bal          | 16.69 | 417   |
| Composite A       | 4                     | 10 Bal          | 16.47 | 398   |
| Composite B       | 8                     | 10 Bal          | 16.06 | 452   |
| Composite C       | 4                     | 20 Bal          | 16.70 | 453   |

3. Results and discussion

3.1. Microstructure and phase components of sintered sample

The density and hardness of sintered samples is listed at Table 1. Vickers hardness of the samples has no apparent changes with the addition of TiB₂. Fig 1 shows the XRD patterns of Ta-W alloys with TiB₂ addition. Two intermetallic compounds, Ta₂B and Ta₃B₂, were distinguished without any diffraction peaks of W observed. The diffraction peaks of Ta have a significant shift to higher angles. It indicates the solid solution has been formed. When part of the larger Ta atoms (atom radius of 209 pm) was replaced by W atoms with a smaller atom radius of 202 pm, decreasing the Ta lattice dimension would result in the shift of the diffraction peaks of the solid solution to higher angles.

![Figure 1. X-ray diffraction patterns of composites and alloy.](image)

Figure 2 represents typical back scattered electron images of Ta-10 W alloy. It is observed that the grain size was around 20µm and white lines were identified as grain boundary. EDS spectrum analysis...
has been shown that the mass ratio of Ta in white parts was 82.3wt% and O occupied 17.7wt% respectively. In the inner part of the grain, only Ta, W were identified with Ta of 82wt% and W of 18wt%. From the results above, it indicates that Ta2O5 were formed during sintering process and enriched at grain boundary.

**Figure 2.** Back scattered electron (BSE) images of Ta-10 W alloy.

**Figure 3.** SEM images of composite and corresponding energy-filtered images.

Figure 3 shows the microstructure of TiB2/TaW composite and corresponding energy-filtered images of Ta, W, Ti, and O. According to elements mapping, Ta and W coexisted at grain, while Ti
and O enriched at grain boundary, indicating that TiO₂ was formed at grain boundary. The EMPA analysis of interested phase is shown in Figure 4. Some needle-like crystals were observed, and from elements analysis, it showed that intermetallic Ta₂B and Ta₃B₃ have been formed. The reaction can be described as following:

\[ \text{Ta} + \text{Ta}_2\text{O}_3 + \text{TiB}_2 \rightarrow \text{Ta}_2\text{B} + \text{Ta}_3\text{B}_3 + \text{TiO}_2 \]  

(1)

![Figure 4. BSE image and EMPA analysis of composite C.](image)

| point | composites |  
|-------|-------------|
|       | Ta | W | B |
| 1     | 69.5 | 1.2 | 29.9 |
| 2     | 55  | 7.9 | 31.5 |
| 3     | 52.3 | 0.67 | 46.9 |

**Table 2.** Mass Gain per Unit in Ta-W alloy and composites during exposure at different temperature

| Material     | Temperature | Mass gain per Unit after 0.5 hour exposure/(mg/cm²) | Mass gain per Unit after 2 hour exposure/(mg/cm²) |
|--------------|-------------|---------------------------------------------------|-------------------------------------------------|
| Ta-10W alloy | 700°C       | 16.3                                              | 42.43                                           |
|              | 800°C       | 13.29                                             | 57.27                                           |
|              | 900°C       | 25.05                                             | 100.81                                          |
| Composite A  | 700°C       | 0.75                                              | 5.87                                            |
|              | 800°C       | 2.35                                              | 15.74                                           |
|              | 900°C       | 18.47                                             | 80.88                                           |
| Composite B  | 700°C       | 0.31                                              | 2.01                                            |
|              | 800°C       | 1.66                                              | 7.92                                            |
|              | 900°C       | 8.75                                              | 34.88                                           |
| Composite C  | 700°C       | 0.43                                              | 1.28                                            |
|              | 800°C       | 1.64                                              | 6.81                                            |
|              | 900°C       | 7.28                                              | 29.21                                           |

3.2. Oxidation behavior

The oxidation kinetics at different temperatures has been studied in terms of the variation in mass gain per unit area with time. The results in Table 2 show the net mass gain observed in the Ta-10W alloy, and composites after 0.5 hour and 2 hour of exposure at 700°C, 800°C, and 900°C. It can be summarized as following:

1. On oxidation at 700°C, mass gain of the alloy is more than about twenty times that of the composite A. In contrast, the mass gain of composite A is almost similar as that of the alloy at 900°C;

2. At 700°C, the composites exhibit mass gain of almost one order of magnitude less than the exhibited by the Ta-10W alloy. The mass gain at 900°C is also less in the composite, compared to that in the Ta-10W alloy, although the difference is not as much as that observed for exposure at 700°C.

Figure 5 shows the curve of oxidation time to mass gain per unit at 700°C. All curves were in good agreement with liner law. After 2hr oxidization, the oxidized layer of alloy spalled from the matrix, and the “pest” oxidation can be observed. While, the oxidized layer of composites remained on the surface. The mass gain of composites ranked consecutively according to the volume fraction of TiB₂.
Figure 5. The mass gain per unit to oxidation time at 700°C.

Figure 6. The mass gain per unit to oxidation time at 800°C (right) and 900°C (left).

The oxidation plots at 800°C and 900°C are displayed in Figure 6. Linear oxidation kinetics is also observed. It is obvious that the mass gain and oxidation rate of TiB₂/Ta-W composites were less than those of Ta-W alloy. Moreover, with the oxidation temperature increasing, the oxidation velocity of TiB₂/Ta-W increased much faster as compared with Ta-W.

3.3. Oxidized scale
The phase component of oxidized layer is shown in Fig 7 via XRD analysis. It indicates that the oxidized layer of Ta-W alloy was mainly composed of Ta₂O₅ without WO₃ identified. The diffraction peaks of Ta₂O₅ shifted to higher angles obviously due to the solid solution effect of WO₃ [7]. And minimal phase of TiO₂ also can be inspected in Ta-W/TiB₂ composites.

The morphology of oxide layer of alloy and composites oxidized at 700°C are shown in Figure 8. The “bubble” crack was observed on the oxidized layer of Ta-W alloy after 0.5 h (see Figure 8a) exposing in air. From the cross section of 2 h oxidized scale (see Figure 8b), the oxidized layer was
separated from the matrix. Crack around grain boundary appeared on the oxidized layer of composite C (see Figure 7c). The more compact microstructure of cross section could be found in oxidized layer of TiB$_2$/Ta-W as compared with Ta-W (see Figure 7d). However, overlapped layer has been formed during oxidation process with cracks and holes between the layers. The linear behavior is attributed by the cracking of oxide layer.

![X-ray diffraction patterns of oxidized layer.](image)

**Figure 7.** X-ray diffraction patterns of oxidized layer.

![Morphology of oxide layer and cross section of Ta-W alloy and composite oxidized at 700°C.](image)

**Figure 8.** the morphology of oxide layer and cross section of Ta-W alloy and composite oxidized at 700°C (a: top surface and b: cross section of Ta-W alloy; c: top surface and d: cross section of composite C).
3.4. Oxidation kinetics

The variation of the oxidation mass gain to time shown in Figure 5 and Figure 6 can be expressed with equation (2):

\[ \Delta W = K \cdot t \]  

where \( \Delta W \) is the oxide mass gain (mg·cm\(^{-2}\)), \( K \) is the oxidation reaction rate constant (mg·cm\(^{-2}\)·h\(^{-1}\)), and \( t \) is the oxidation time. Table 3 shows the constant \( K \) of linear oxidation rate for alloy and composites at all oxidation temperature. The activation energy was determined by Arrhenius equation. The Ta-W alloy showed very weak oxidation behavior at 700°C. The addition of TiB\(_2\) increased the oxidation resistance. From calculated results of activation energy of Ta-W alloy and the composites, it shows that Ta-W alloys present lower oxidation activation energy than that of TiB\(_2\)/Ta-W composites. The higher activation energy could be used to explain sensitive effect of temperature on TiB\(_2\)/Ta-W composites.

| Table 3. oxidation activation energy of alloy and composites |
|------------------------------------------------------------|
| Sample name      | \( K \) (mg·cm\(^{-2}\)·h\(^{-1}\)) | 700/(°C) | 800/(°C) | 900/(°C) | \( E_a \) (kJ·mol\(^{-1}\)) |
|------------------|---------------------------------|----------|----------|----------|-----------------|
| Ta-10W           | 4.04                            | 30.83    | 52.97    |          | 116.1           |
| Ta-10W-4TiB\(_2\)| 1.99                            | 9.29     | 38.15    |          | 134.0           |
| Ta-10W-8TiB\(_2\)| 1.21                            | 4.42     | 17.07    |          | 141.4           |
| Ta-20W-4TiB\(_2\)| 0.51                            | 3.20     | 13.7     |          | 152.2           |

It can be concluded that Ta-W alloy is continuously oxidized during the oxidation process due to none stable protective oxide scale formed, [8]. With cracking of the oxide scale, more surface area can be supplied for oxidation and the penetration of oxygen to the alloy beneath is allowed. But, if cracking was accompanied by spallation, a mass reduction would be occurred in the natural consequence. In case of TiB\(_2\)/Ta-W composites, a stable TiO\(_2\) has been formed to hinder oxidation efficiently. Liquid B\(_2\)O\(_3\) benefits the adhesion of oxidized layer with matrix at lower temperature, while, a quick oxidation volatility of B\(_2\)O\(_3\) is accomplished at high temperature. It will cause more defects in oxidized layer [6]. The stable TiO\(_2\) will be damaged at about 1070K [9]. Therefore, constantly destroying of TiO\(_2\) at 800 °C and 900 °C causes cracks and defects in the oxide layer which allow oxygen entering to the inner surface with further oxidation occurred.

4. Conclusions

TiB\(_2\)/Ta-W composites have been prepared by hot-press sintering methods. The intermetallic compounds Ta\(_2\)B and Ta\(_3\)B\(_2\) have been distinguished in composites with TiO\(_2\) enriched in grain boundary. TiB\(_2\) additive benefits to oxidation resistance of Ta-W alloy, especially at lower temperature. Oxidation kinetics curves of TiB\(_2\)/Ta-W composites obey liner law due to none stable protective oxide scale formed.

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