Research about Titanium Alloyed Layer's Temperature Oxidation Resistance on Aircraft Engine Surface

Ao Huang [1], Jie Yang [2], Yulong Zhang [1] and Lei Jin [1]

[1]2017 Graduate student in Southwest Forestry University, Kunming, Yunnan, 650224, China

[2] School of mechanical and manufacturing engineering, Southwest Forestry University, Kunming, Yunnan, 650224, China

[*] Corresponding author's e-mail: 351725623@qq.com

Abstract: Aircraft engines often work in a high temperature or easily oxidized environment, and the titanium alloy layer on the surface of the existing aircraft engine is poorly resistant to high temperature oxidation. The maximum temperature that can bear currently is slightly above 500°C, which severely limits its widespread application. In order to improve its resistance ability to high temperature oxidation, laser surface alloying technique was adopted here which Ti-Al-xSi alloying layer was prepared on the surface of matrix Ti-6Al-4V alloy (It is mainly composed of Ti-Al Intermetallic Compound and Ti5Si3 Reinforced Phase) and the analysis were presented in three aspects: material phase, tissue observation and high temperature oxidation resistance ability during different time periods. The experimental data of tissue composition, structure and high temperature oxidation resistance of Ti-al-xsi alloying layer which was preset different proportion of Al powder and Si powder mixture were compared. The experimental results showed that, when the mass of Si powder was 10%, 20% and 30% of the Al powder mass, Ti-Al Intermetallic Compound has evolved from TiAl to TiAl2 phase and TiAl3 phase with the increasing additive amount of Si, which had excellent oxidation resistance at high temperature. At the same time, the oxidation weight of alloying layer was decreased and the oxidation rate was declined.

1. Introduction

Titanium and its alloys are widely used in the fields of aerospace, military industry, metallurgy, seawater desalination, light industry, environmental protection, chemical industry and medical equipment medicine because they have high specific strength, low density, good corrosion resistance, stable strength at medium temperature, non-magnetic, easy processing, forming and welding, and they have four unique functions of shape memory, superconductivity, hydrogen storage and biocompatibility. Among many countries around the world, Chinese titanium reserves rank first in the world, which have strong titanium resource advantage and complete titanium industrial production capacity, and it is the fourth largest titanium industrial country after the United States, Russia and Japan [1-3]. Up to now, there are over 100 kinds of known titanium alloys, but only 20-30 kinds have reached the level of commercial application.

Among the titanium and titanium alloys, the chief representative is Ti-6Al-4V alloy, which accounts for more than 50% of the total titanium application [4-6]. With the improvement of aircraft performance and thrust-weight ratio of aero-engine in the aviation industry, the amount of titanium and titanium alloy increases gradually. Among foreign advanced aero-engines, the amount of titanium alloy has accounted for 25% - 40% of the total engine.

The incapability of anti-high temperature oxidation of titanium and titanium alloy restricts its maximum temperature of long-term service [7]. Exampled by the most widely used Ti -6Al- 4V in the aviation industry, whose long-served highest temperature is 350 ℃ and which can only be used in the manufacture of aircraft engine operating temperature lower fan blades and compressor 1, level 2 blades [8-9].

2. Experiment

2.1. Test materials

Titanium alloy Ti-6Al-4V: Ti-6Al-4V is a (α＋β) type alloy developed by Illinois Research Institute of the United States, which has good technological properties. It is the most deeply studied and mostly tested alloy at present, so it is widely used in the aviation field. The Ti-6Al-4V alloy with a size of 10mm * 10mm * 10mm was used as laser surface alloying specimen. The laser surface is sanded by sandpaper before laser treatment and then put into acetone for ultrasonic cleaning. Al powder and Si powder were selected as laser surface alloying powder materials. The alloying powder was proportioning in different proportions and grinded in the mortar to mix evenly. The mixed alloyed powder was placed in a vacuum drying box before laser surface alloying and then dried at 180 C for 10 minutes.

2.2. Laser surface alloying equipment and preparation process

The laser surface alloying technology is carried out on the TJ-HL-5000 cross flow multi-mode CO2 continuous laser facility. Al-Si alloyed mixed powder was pre-placed on the surface of Ti-6Al-4V alloy sample by using a self-made slot with a specific height, and the pre-placed powder height was controlled between 0.8 and 1.0 mm. On the basis of the previous experimental results, the optimum parameters of laser surface alloying process are laser power 3-3.5 kW, scanning speed 30 mm/min and laser spot size 10 mm *1 mm. Laser surface alloying is carried out in a semi-enclosed self-made container with argon as a protective gas. The method of laser surface alloying for samples of size 10mm x 10mm x 100mm is as follows: Single laser surface alloying was performed on a 10mm x 100mm surface after grinding，then linear cutting， cutted into 10mm x 10mm x 10mm size and used for phase analysis, tissue observation and high temperature oxidation resistance analysis of alloying layer.

2.3. Organize performance analysis and test methods

The surface or cross section of the alloyed samples were polished by 280 mesh, 600 mesh, 1200 mesh and 2000 mesh metallographic sandpaper respectively, and then cleaned with alcohol. The cross section was corroded by HF:HNO3:H2O=2:1:17 corrosive solution. The microstructure of the sample surface and cross section was observed by SEM, and the composition of the sample surface and cross section was qualitatively and quantitatively analyzed by EDS. The high temperature oxidation cycle test of the sample was carried out at a temperature of 800 degrees in a box type resistance furnace. The length, width and height of the sample were measured with vernier calipers, then the surface area of each surface was calculated, then weighed together with the crucible on the electronic scale and recorded the starting weight. Then weighed together with the crucible every 20 hours, total weighed five times. The oxidation weight gain of the sample per unit surface area was calculated at 20 h, 40 h, 60 h, 80 h and 100 h, respectively. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to observe the phase composition and morphology of the aStudy on Microstructure and properties of 2 Ti-Al-xSi alloying layer after oxidation in five different stages.

3. Study on Microstructure and properties of Ti-Al-xSi alloying layer

According to the test plan, we need to carry out SEM and X-ray diffraction experiments. The tissue composition, the structure of the organization and oxidation morphology of Ti-Al-xSi alloyed layers with different percentage composition were compared. Tissue composition, tissue structure and oxidation morphology at different time periods were studied.

3.1. Preparation of Ti-Al-xSi alloying layer

On the surface of Ti-6Al-4V alloy, the mixed powder composed of Al powder and Si powder is preset. Among them, the content of Si in the mixed powder is 10%, 20% and 30% of Al powder, respectively. The corresponding laser surface alloying layers are named as Ti-Al-10Si, Ti-Al-20Si and Ti-Al-30Si alloying layers.

3.2. the structure of Ti-Al-xSi alloying layer

Fig. 1 is the X-ray diffraction pattern of Ti-Al-xSi alloying layer. Table 1 is the Gibbs free energy of Ti-Si binary system at different temperatures. The results show that the Ti-Al-xSi alloying layer is mainly composed of Ti-Al intermetallic compound and Ti5Si3 intermetallic compound. The Ti-Al intermetallic compound in the Ti-Al-10Si alloying layer is TiAl, while the Ti-Al intermetallic compound in the other Ti-Al-xSi alloying layer includes not only TiAl but also TiAl3. The peak strength of TiAl3 phase increases with the increase of Si content in the alloying layer. Ti and Si can form many Ti-Si intermetallic compounds at high temperature, such as Ti5Si3, Ti5Si4, TiSi and TiSi2. According to thermodynamic data, Ti and Si have the lowest free energy to form Ti5Si3 compared with other Ti-Si intermetallic compounds, so Ti5Si3 is the easiest to form in thermodynamics. Therefore, with the increase of Si addition, the peak strength of Ti5Si3 phase in the alloying layer also increases. In addition, the TiAl3 phase is also mainly present in the alloying layer with high Si addition. This is mainly due to the fact that the melting point of Ti5Si3 is 2130 Celsius, while the melting point of Ti-Al intermetallic compound is only 1340-1600 Celsius. Ti5Si3 phase will be formed preferentially in the early stage of crystallization. With the increase of Si addition, Ti5Si3 phase's peak strength in alloying layer increases.

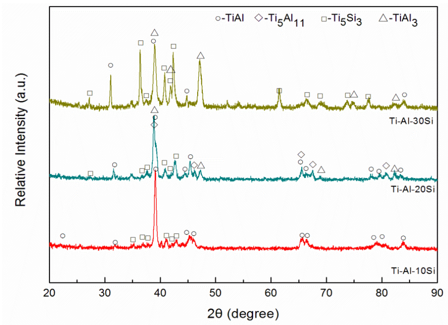

Figure 1. X ray diffraction pattern of alloying layer of Ti-Al-xSi system

Table 1. Gibbs free energy of Ti-Si two element system at different temperatures

	1000K	1200K	1400K	1600K	1800K	2000K
Ti+Si=TiSi	-129.202	-129.102	-129.002	-128.902	-128.802	-128.702
5Ti+3Si=Ti_5Si_3	-587.366	-589.026	-590.686	-592.346	-594.006	-595.666
5Ti+4Si=Ti_5Si_4	-335.776	-338.096	-340.416	-342.736	-345.056	-347.376

The SEM morphology of Ti-Al-xSi alloying layer and EDS composition analysis results. The alloying layer of Ti-Al-xSi is dense and the thickness is between 870 and 1040 μ m. The middle part of Ti-Al-xSi alloying layer is uniform with the upper part, while the composition at the bottom changes in gradient, which conforms to metallurgical bonding characteristics. It can be seen by local magnification of the alloying layer, the morphology of Ti-Al-xSi alloying layer is basically similar.

4. High temperature oxidation behavior of Ti-Al-xSi alloying layer at 800 C

4.1. Oxidation products of Ti-6Al-4V matrix and Ti-Al-xSi alloying layer

The XRD patterns of the Ti-6Al-4V alloy matrix coating after 100h oxidation and the oxidation XRD patterns of the Ti-Al-xSi alloy are shown in Fig. 2 and 3. It can be seen from the matrix diagram that after 10 minutes of oxidation, the oxide peaks dominated by the rutile structure TiO2 were formed on the surface of the alloy, while few oxide peaks of Al2O3 were formed. This oxide structure is caused by the low aluminum content of Ti-6Al-4V alloy.

Ti - Al - xSi alloying layer oxidized in the 800 °C for 100 hours, at the initial stage of oxidation, both TiO2 and Al2O3 nucleated and grew on the surface at the same time. With the prolongation of oxidation time, the intensity of phase peaks of TiO2 is significantly higher than that of Al2O3, which indicates that the growth kinetics of TiO2 phase is much greater than that of Al2O3. The oxidation products of Ti-Al-xSi alloying layers were mixed oxides of TiO2 and Al2O3 after oxidation at 800 C for 100h. No single Al2O3 oxide film was found. Because of the different addition of Si, the phase structure of the oxide film on the alloying layer is also different. The phase peaks of Ti-Al-10Si and Ti-Al-20Si alloyed layers disappeared after 100 h of oxidation, indicating that the oxide film thickness formed at this time has reached the detection limit of X-ray. The peak of Ti5Si3 phase in Ti-Al-30Si alloy layer is still obvious after 100h oxidation, which indicates that the thickness of oxide film is very thin and the oxidation rate is slow. The phase peak of SiO2 was not found in all Ti-Al-xSi alloying layers. Ti5Si3 is very stable at high temperature without decomposition, but the following oxidation reactions will occur.

$$Ti_5Si_3(s) + 8O_2(g) = 5TiO_2(s) + 3SiO_2(s) \quad (1)$$

Therefore, the surface of Ti5Si3 will form both TiO2 and SiO2 during oxidation, but the diffraction peaks of SiO2 have not been detected in this paper, indicating the formation of amorphous SiO2。

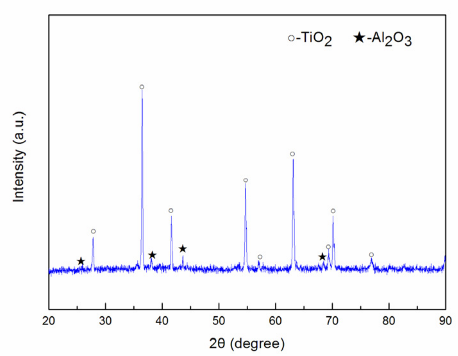

Figure 2. XRD diagram of oxidation of Ti-6Al-4V alloy substrate

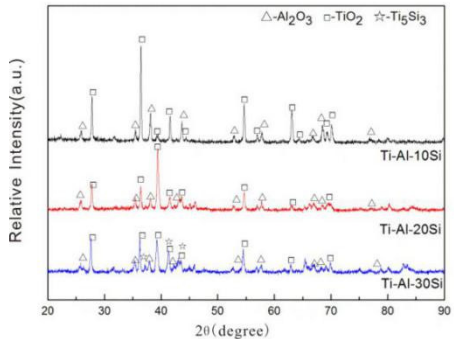

Figure 3. X ray diffraction pattern after oxidation of Ti-Al-xSi alloy alloying layer

4.2. Oxidation kinetics of Ti-Al-xSi alloying layer

Tables 2 and 4 show the kinetic curves of oxidative weight gain and oxidation kinetics per unit surface area of Ti-Al-xSi alloyed layer and substrate at 800℃. Fig 5 shows the kinetic curves of oxidative weight gain and oxidation kinetics per unit surface area of Ti-Al-xSi alloyed layer at 800℃. The weight gain of Ti-Al-10Si、Ti-Al-20Si and Ti-Al-30Si alloyed layers oxidized at 800℃ for 100 h were 4.24408 mg/cm 2 and 3.56198 mg/cm 2, respectively.

Table 2． The oxidation of unit and surface area of matrix and three alloying layers in 100h increases

Time	Ti-6Al-4V	Ti-Al-10Si	Ti-Al-20Si	Ti-Al-30Si
0	0	0	0	0
20h	7.48333	1.90138	1.49284	1.46474
40h	11.61667	2.72837	2.127	2.0989
60h	17.53333	3.25895	2.66474	2.66061
80h	22.43333	3.79972	3.17493	3.10854
100h	28.95	4.24408	3.56198	3.53802

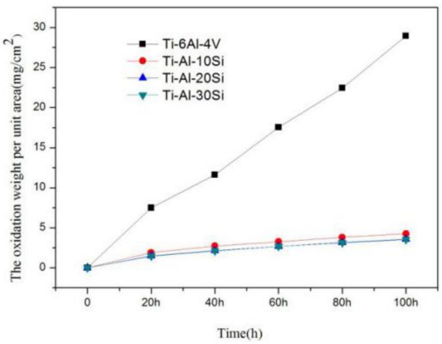

Figure4. Oxidation kinetics curves of matrix and Ti-Al-xSi alloying layer at 800 C

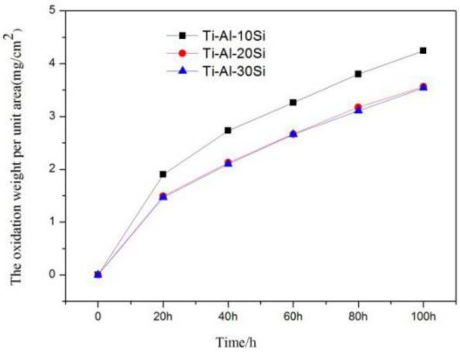

Figure5. Oxidation kinetics curves of Ti-Al-xSi alloying layer at 800 C

Compared with Ti-6Al-4V oxidation at 800C for 100h, the oxidation weight gain of Ti-6Al-4V and Ti-6Al-4V were 28.95mg/cm 2 and 1/7, 1/8 and 1/9 respectively. The addition of Si and Al can effectively reduce the oxidation rate of the alloying layer and provide effective protection for the alloying layer.

As can be seen from Fig. 4, the alloyed layer gains weight faster at the beginning and slower later, due to different control factors in the oxidation process. It can also be seen from Figure 4 that the oxidation weight gain decreases with the increase of Si addition in the alloying layer, this is mainly due to the addition of Si to the alloying layer to form Ti5Si3 phase, in addition, the Ti5Si3 phase can form amorphous SiO_2 with good density and adhesion in the process of oxidation; High Si content promoted the formation of $TiAl_3$ phase with excellent oxidation resistance in the alloying layer.

5. Conclusion

The histological composition, histological structure and high temperature oxidation resistance during different time stages of ti-al-xsi alloying layer with different percentages were compared through the Data obtained through experiments.

In this paper, the microstructure, structure, oxidation morphology and high temperature oxidation resistance behavior of Ti-Al-xSi alloyed layers with different Si content were analyzed. The microstructure and properties of Ti-Al-xSi alloyed layers on laser surface of titanium alloys were studied and the Ti-6Al-4V alloy was prepared by metallography, the structure, composition and oxidation morphology of Ti-6Al-4V alloy were observed and measured the high temperature oxidation resistance of alloying layer with different Si content was measured. The conclusions are as follows: the alloying layer of Ti-Al-xSi is mainly composed of Ti-Al intermetallic compound and Ti_5Si_3 reinforced phase. With the increase of Si content in the alloying layer, the TiAl phase evolves into $TiAl_2$ and $TiAl_3$ phases.

The product of the Ti-Al-xSi alloy layer oxidized at 800 C for 100h was a mixture of TiO_2 and Al_2O_3. The oxidation adds weight was one tenth of that of the matrix, showing excellent high temperature oxidation resistance. With the increase of Si addition, the oxidation weight gain of alloying layer is smaller. The high-temperature oxidation resistance of the alloyed layer was significantly improved with the addition of Si, mainly because: (1) Ti_5Si_3 phase was formed when Si was added into the alloyed layer, and amorphous SiO_2 with good compactness and adhesion was formed on the surface of the alloyed layer during the oxidation process of Ti_5Si_3 phase; and (2) the high Si content promoted the formation of the $TiAl_3$ phase with excellent high temperature oxidation resistance in the alloying layer.

Project Number: C17183

Reference

[1] Shao Dechun, Li xin. (1997) Improvement of high temperature oxidation resistance of titanium alloy by laser surface alloying[J]. Chinese laser, 24(3): 281-285.
[2] Jia Weiju, Zeng Weidong, Liu Jianrong, Wang Qingjiang, Zhou Yigang. (2010) Oxidation behavior of Ti60 high temperature titanium alloy[J]. Rare metal materials and Engineering, 39(5): 781-786.
[3] Jia Xinyun, Liu Peiying, Tao ye, Guo Baolin. (2000) High temperature oxidation and protection of titanium alloys[J]. Aernautical Engineering and maintenance, (4): 19-21.
[4] Zeng Sangwu, Jiang Haotao, Zhao Aimin. (2015) High temperature oxidation behavior of TC4 titanium alloy[J]. Rare metal materials and Engineering, (11): 2812-2816.
[5] Shao juan. (2007) Research progress of titanium alloys and their applications[J]. Rare Metals and Cemented Carbides, 35(4): 61-65.
[6] Wang yan, Li xin, Sun Yujing, Fu Xiaoliang. (2013) Research progress in the patents of laser surface modification of titanium alloys[J]. Electronic production, (15): 237-238.
[7] Zhou wei. (2005) Aluminizing treatment and high temperature oxidation on titanium alloy surface[D]. Changchun: Jilin University.
[8] C.Zhou, F.Cai, H.Xu, S. Gong. (2004) Cyclic oxidation behavior of Al-Cu-Fe-Cr quasicrystalline coating on titanium alloy [J]. Materials Science & Engineering A, 386(1-2): 362-366.
[9] S. Y. Hui, X. Zu, J. S. Xiao and G. S. Yuan. (1999) Influence of Nb Ion Implantation on Oxidation Resistance of High Temperature Titanium Alloy at 650 °C[J]. Rare Metals, 18(3): 165-166.