Effects of the Microstructure and Mechanical Properties on Ti6Al4V2Cr with Nd Element Additions

Ji-Yao LIU¹, Wen-Yan WANG¹,²,a,*, Ya-Bo HUANG¹, Hao-Yin ZHANG³, Wen-Jun HUANG¹, Shi-Qin SHI¹ and Jing-Pei XIE¹,²

¹Henan University of Science and Technology Material Science and Engineering, China Luoyang Henan 471003
²Collaborative Innovation center of Nonferrous Metals Henan Province, China Luoyang Henan 471003
³College of Material, Xiamen University, China Xiamen Fujian 361005

a wangwy1963@163.com
*Corresponding author

Keywords: Rare Earth, Phase Boundary, Fine Grains, Tensile Strength, Elongation.

Abstract. Titanium alloy in this experiment was prepared by powder metallurgy method, which could reduce the production cost and eliminate the composition segregation effect on titanium alloy. After heat treatment, microstructure and phase structure of the Ti-6Al-4V-2Cr-xNd was analyzed by microscope, XRD and TEM. The rare earth oxide particles dissolved out from the phase boundary and phase could purify matrix and fine grains, leading to the improvement of tensile strength and elongation by 10.7% and 49.1% respectively.

Introduction

In the case of the USA began its fourth hypersonic aircraft test, China also began testing self-developed hypersonic aircraft. Hypersonic vehicle is considered the next generation technology, flight speed of which is more than 10,000 km/h (close to Mach 9.6). With the development of the space industry and spacecraft rate, traditional Mg-based alloys and Al-based alloys have been increasingly unable to meet the design requirements, titanium alloy with high specific strength, high stiffness ratio and excellent high temperature resistance has become the first choice material[1-3].

In this paper, powder metallurgy was adopted to prepare titanium alloy, which can reduce the production cost and eliminate the impact of segregation on the alloy properties. Besides, rare earth element Nd was added in Ti-6Al-4V-2Cr to improve its property. Low negative potential of the rare earth chemical makes it has more affinity with oxygen than titanium[4], which means that during the sintering process it will take away the oxygen from the titanium, then precipitated in the grain boundary, thereby improving the mobility of titanium powder in sintering. Also, solution of rare earth elements in the grain interior can precipitate from crystal for further crystal purification, forming a finer, flaky and mutually staggered $\alpha + \beta$ phase. The small $\alpha + \beta$ phase s plays an important role in preventing fatigue crack extension, improving the life of fatigue crack and inhibiting the precipitation and growth of the Ti$_3$Al. It is also worth mentioning that adding the Nd can achieve the purpose of improving the tensile strength and elongation at room temperature.

Materials and Methods

Preparation of the Sample

In this paper, the Blended Element was adopted to prepare the PM sample. The Blended Element started to be used in the 1980s, now it has become one of the major methods to prepare the powder metallurgy titanium[5,6]. In this method, the titanium alloy powder and other alloy powder is well mixed initially, and green compact was prepared by cold isostatic pressing or press molding.
Finally, the green compact was sintered in a vacuum furnace.

Adding the rare earth element usually use the method of adding rare earth alloy compound, the disadvantage of this method is that the rare earth elements cannot greatly absorb oxygen impurity element contained in the substrate. In this paper the Nd was added directly. Since the Nd is active and can be easily oxidation, Ar was used as protective atmosphere during mixing. Ar can sink in the bottle when poured into a mixing bottle because it is heavier than air, so Ar can greatly protect the Nd from being oxidizing. Mixing was carried out in a Y-type mixing machine for 24h. The well mixed powder was pressed by cold isostatic pressing at a pressure of 280 MPa for 30min and sintered in a vacuum sintering furnace at a temperature of 1300 °C for 3h (degree of vacuum is 1×10⁵ Pa). And then the sample would be cut for heat treatment experiment, mechanical test and microstructure analysis.

Results and discussion

Analysis of the Ti-6Al-4V-2Cr-xNd’s Tissue Composition

Figure 1 shows microstructure of samples with different Nd content (1%, 1.5%, 2% and 2.5%). Former studies show that when the contents of RE is less than 1%, it is difficult to observe morphology of precipitation since there is little precipitates and the mechanical properties of the alloy shows an upward trend with the increase in RE content[7,8]. Therefore, the starting amount of this test is the minimum content of 1%, researching the influence of the RE content on the microstructure and properties of Ti-6Al-4V-2Cr.

Structure of the alloy is solution aging state, heating treatment process is 920 °C×50 min(WQ)+aging 460 °C×8 h(WQ). After the solution treatment in 920 °C, metastable supersaturated solid solution can be obtained. The aging process will make precipitate precipitates from the supersaturated solid solution, and the dispersed precipitate will strengthen the matrix. Fig.1 is the optical microstructure of Ti-6Al-4V-2Cr alloys with different content of Nd.

From Fig.1, it can be seen that Nd has great impact on alloy’s structure. With the increase of Nd, the alloy is combined by the interlayer β transition phase, lamellar α phase and primary α phase. It can also be seen that there is a sheet, finer and staggered α+β phase, the grain size of which is about 10μm. Such a fine α + β lamellar structure could increase the density of grain boundary, playing an important role in preventing the growth of fatigue crack. Nd can reduce the forming difficulty of α phase and increase the amount of α phase in sintering process, because Nd is a stability element. After solid solution aging, secondary α phase heated volume obviously become larger. As shown in Fig.1-d, with the increasing content of Nd, secondary α phase obviously increase and become larger.

In sintering process, Nd and the oxygen in the matrix can act with each other and form rare earth oxide particle with high melting point and stable chemical properties. When oxide separates out in the phase boundary, it can eliminate the oxidation film on the particle surface in the process of powder metallurgy sintering, promoting sintering and increasing sintering density. However, with the increase of the content of Nd, a large number of refractory rare earth oxide particles are formed. They can hinder the combination of grains, although they can inhibit the growth of grain.

It can be seen from Fig.1 that the amount of hole is increased with an increase in Nd content, which has a serious influence on the mechanical properties of the material.
The Analysis of the Ti-6Al-4V-2Cr-xNd’s Mechanical Property

The secondary phase particles precipitated on the grain boundaries have a certain degree of separation of the matrix. And the bonding strength between these particles and the matrix is not high, leading to grain boundary embrittlement. At the same time, Nd$_2$O$_3$ is precipitated as resource of crack which will lead to the intergranular fracture. The precipitated second phase particles are the source of dislocation, and also the obstacles to the movement of dislocations. The second phase can hinder the sliding of grain boundary and phase boundary, which can improve the tensile strength of the alloy. In the sintering process, rare earth elements absorbed the oxygen in the crystal, dispersed second phase and largely refined grain size, obviously improving the tensile strength and elongation. It can be seen that the effect of the rare earth on the tensile strength of titanium alloy is very complicated.

For Ti-6Al-4V-2Cr, the mechanical properties of samples with different content of Nd (0% means did not add Nd) were tested in the heat treatment state as shown in Fig.2.

As shown in the Fig.2, when the content of Nd increased from 1%-2.5%, the mechanical property of the samples with Nd added is much better than those with no Nd. With the increasing content of Nd, tensile strength and plasticity decline significantly. It is thought three factors lead to this phenomenon:

First, in the sintering process, formation of Nd$_2$O$_3$ increases the nucleation rate, raises the diffusion activation energy and inhibits the growth of nucleation. According to the Hall-petch Formula[9].

$$\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}}$$

$\sigma_y$ is the yield strength, $\sigma_0$ is the friction force required for a single dislocation movement, $K_y$ is the constant, d is the average size of the grain.
From the formula, we can find that the yield strength is inversely proportional to the grain size. The addition of Nd refined grain size obviously and increased yield strength significantly. Meanwhile, small particles can also increase the elongation of the material.

Second, from Fig.2 it can be seen that the addition of Nd reduces the difficulty to form the $\alpha$ phase in the sintering process, which makes more $\alpha$ phase separate out. With the increasing content of the Nd, primary $\alpha$ phase obviously become larger. As a result, when the alloy is under stress, the slip can pass through the coarse primary $\alpha$ phase easily[10] and form the dislocation accumulation in the phase boundary, leading to uneven deformation in micro region. Hence, crack source forms and lead to fracture.

Finally, with the increase of Nd, more Nd$_2$O$_3$ will be formed. A certain amount of the Nd$_2$O$_3$ can purify grain boundary and promote the sintering process. However, too much Nd$_2$O$_3$ separated out at grain boundaries will make sintering cannot be carried out smoothly, since the melting point of rare earth precipitates is higher than sintering temper. From Fig.1, it can be seen that the number of pores increases obviously.

**The Phase Analysis of Ti-6Al-4V-2Cr-1Nd**

The Ti-Nd phase diagram shows that Nd has a large solubility in the Ti under high temperature. The solubility of Nd in the Ti is about 4.8% (wt %) when the temperature is 1300 °C. Although oxygen is bad for the mechanical properties of titanium alloy, titanium powder in the powder sintering samples inevitably contain a certain amount of oxygen element. Nd diffuses in Ti matrix easily during the process of sintering. In the process of furnace cooling, Nd will combine with O in Ti matrix, thus forming the Nd$_2$O$_3$.

Figure2-3 is X-ray diffraction (XRD) results of Ti-6Al-4V-2Cr-1Nd alloy. In addition to $\alpha$-Ti and $\beta$-Ti in the alloy, the main deposition Nd$_2$O$_3$, a small amount of Nd and Nd$_2$Ti$_3$O$_{11}$ can be found in the pattern. Existence of Nd indicates that Nd did not react with oxygen in the air under the protection of Ar during the process of mixing, pressing and sintering. Therefore, oxygen contained in Nd$_2$O$_3$ was absorbed by Nd from the matrix alloy during the sintering process. It shows that the atmosphere protection of sintering and mixing process is successful.
Analysis of Ti-6Al-4V-2Cr-1Nd Precipitation Phase by Projection Electron Microscope

After adding a certain amount of rare earth elements in the alloy, the existence and unique properties of rare earth elements in titanium alloys can affect the solubility of impurity elements in the matrix, resulting in the increase of grain boundary precipitates. Additionally, the rare earth elements with solid solution can be separated from the phase, and further purified the crystal.

Ellipsoidal precipitates are also found inside the phase. Figure 4-b is found to have two sets of diffraction spots. By using JCPDS card calibration, it is found that the light spots are the matrix $\beta$-Ti (JCPDS44-1288, Body centered cubic structure), $a=3.306$. The other set of diffraction spots are $\text{Nd}_2\text{O}_3$ (JCPDS28-0671, Single crystal system), $a=14.32$, $b=3.28$, $c=9.02$, $(90\times100.45\times90)$, $\beta$-Ti[001] // $\text{Nd}_2\text{O}_3$[100], and $(110)\beta$-Ti // $(003)\text{Nd}_2\text{O}_3$, mismatch degree is 6.4%, both interfaces are semi-coherent interface.

By means of diffraction pattern calibration, it was found that Nd could react with oxygen in the matrix to form $\text{Nd}_2\text{O}_3$ under the protection of Ar during the sintering process. During the sintering process, second phase particles gathered at the interface and precipitated as spherical particles when its density reached nucleation density. Most of the second phase particles were distributed along the grain boundaries, fining grains by pinning effect. There was also a small amount of them distributed inside the grain, acting as nucleation center. In this way, grain size would be decreased due to the increase of nucleation rate. The $\text{Nd}_2\text{O}_3$ presents strong stability, since it was not dissolved in the solid solution aging process and the particle size was unchanged.
Conclusion

When mass fraction of Nb is 1% (i.e. Ti-6Al-4V-2Cr-1Nd), the tensile strength and elongation of the alloy are promoted obviously. The number of holes in the alloy increases with the increase of the content of Nd. The results show that the tensile strength and elongation of the alloy were increased due to the decrease in grain size, leading to the improvement of tensile strength and elongation by 10.7% and 49.1% respectively.

XRD pattern of Ti-6Al-4V-2Cr-1Nd shows that the precipitates have Nd$_2$O$_3$, a small amount of Nd and Nd$_2$Ti$_4$O$_{11}$ phase. Existence of Nd indicates that Nd did not react with oxygen in the air under the protection of Ar during the process of mixing, pressing and sintering. Therefore, oxygen contained in Nd$_2$O$_3$ was absorbed by Nd from the matrix alloy during the sintering process. It shows that the atmosphere protection of sintering and mixing process is successful.

The morphology of precipitates was observed by transmission electron microscope, and the selected electron diffraction pattern area was calibrated. Results from the calibration indicate that Nd$_2$O$_3$ precipitates both at the phase boundary and inside the phase. And the precipitates are parallel to matrix, forming the semi-common interface. Most of the spherical second phase particles are distributed along the phase boundary, fining grain size by the pinning effect. A small amount of particles can be found distributed inside the grain, acting as nucleation center. Grain size would be decreased due to the increase in nucleation rate. The Nd$_2$O$_3$ was not dissolved in the solid solution aging process and the particle size was unchanged, which presents that it has strong stability.

Reference

[1] Liu Yong, Tang Hui-ping. Powder metallurgical titanium base structure materials [M]. Changsha: Central South University Press. 2012: 100-103.

[2] Zhou Wei, Ge Peng, Lu Ya-feng, et al. Research on grain growth behavior of a novel beta titanium alloy on heat treatment[J]. Titanium Industry Process. 2012, 29(5): 23-26.

[3] Xiao Zhi-yu, Li Yuan, et al. Densification mechanism of warm compaction in powder metallurgy[J]. Materials Science and Engineering of Powder Metallurgy. 2006, 11(2): 85-90.

[4] Xiao Dai-hong, Yang Bao-gang, Shen Ting-ting, et al. Effects of Mo, V and Ag additions on microstructure and mechanical properties of powder metallurgy Ti-5Al alloy[J].The Chinese Journal of Nonferrous Metals, 2011, 21(6): 1265-1271.

[5] Hou Hong-liang, Lin Zhi-qiian, Wang Ya-jun, et al. Technology of hydrogen treatment for titanium alloy and its application prospect[J]. The Chinese Journal of Nonferrous Metals, 2003, 13(3): 533-549.

[6] Tang Hui-ping, Huang Bo-yun, Liu Yong, et al. Research progress in the densification of powder metallurgical titanium alloys[J].Rare Materials and Engineering, 2003, 32(9): 677-680.

[7] Ma Ying-jie, Liu Jian-rong, Lei Jia-feng, et al. Effect of titanium alloy β grain growth law and grain size on damage tolerance properties[J]. Rare Materials and Engineering, 2009, 38(8): 976-978.

[8] Wang Liang, Shi Hong-pei. Powder metallurgy technology of high performance titanium alloy[J]. Aerospace Materials & Technology, 2003, (6): 42-46.

[9] Wang Hui, Tang Hui-ping, Liu Yong, et al. Hot deformation behavior and processing maps of as-cast TiAl based alloy[J]. Materials Science and Engineering of Powder Metallurgy 2012, 17(4): 401-407.

[10] Pan Ning, Song Bo, Zhai Qi-jie, et al. Effect of lattice disergisty on heterogenous nucleation catalysis of liquid steel[J].Journal of University of Science and Technology Beijing. 2012, 32(2): 180-182.