

## Effect of Mo, V and Zr on the microstructure and mechanical properties of Ti<sub>2</sub>AlNb alloys

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**Abstract** Small button ingots of Ti<sub>2</sub>AlNb alloys with different contents of Mo, V and Zr were melted by vacuum non-consumable arc furnace. Due to the rapid cooling rate during melting process, only  $\beta$  grains without precipitation were observed in most of the button ingots and no regular phenomenon was found. However, when the samples were heated to  $\beta$  phase region and then furnace cooled to room temperature, different morphologies and quantities of primary  $\alpha$  phase and second O phase formed from the  $\beta$  grains of different samples. It is suggested that the morphology of  $\alpha$  phase was changed from lamellar to quadrilateral with increasing V and the lath O increased with increasing Zr. Besides, the residual  $\beta$ /B2 phase increased with increasing Mo and V. The EDS results showed that Al and Zr were enriched in  $\alpha$  phase whereas Nb, Mo and V were enriched in  $\beta$ /B2 phase. The micro-hardness of these samples before and after heat treatment was detected and the micro-hardness increased with increasing Zr and decreasing Mo and V.

**Keywords:** Ti<sub>2</sub>AlNb alloys, heat treatment, microstructure, hardness

### 1. Introduction

Ti<sub>2</sub>AlNb-based alloys have been extensively studied due to their excellent specific strength and good oxidation resistance at 650~750 °C[1-3]. These advantages made them prospective material to replace high-temperature titanium alloy and superalloy in the field of engineering application. However, the weakness in fracture toughness and creep resistance significantly limited the development and application of Ti<sub>2</sub>AlNb-based alloys at present. Although great effort has been performed by optimizing the hot working and heat treatment process, only limited improvement was achieved over the past years. Therefore, alloying is considered another potential method to promote the combination property of Ti<sub>2</sub>AlNb alloys.

In the study performed by Tang et. al[4, 5], Mo and W were used to replace the Nb in Ti-22Al-27Nb alloy. The results showed that V was effective in improving room temperature ductility, and W was effective in enhancing high-temperature tensile strength and creep resistance. Emura et. al[6] studied the effect of Mo and Fe on the room-temperature ductility of Ti<sub>2</sub>AlNb alloy, and a higher tensile elongation at room temperature was obtained. The effect of Zr on the microstructure and properties was investigated by Germann[7], and it is suggested that the oxidation resistance and creep property were obviously increased when the content of Zr was up to 2 at.%. Besides, the effect of Ta[8], Si[7], B[9] on the phase transformation and mechanical properties was also studied. Notably, most of these works have been done by adding one or two elements into the Ti<sub>2</sub>AlNb based alloys, few studies focused on the simultaneous and commutative effect of three or more elements on the phase transformation, microstructure and the relevant properties.

In fact, according to the development and application of superalloy, the generation and the operating temperature is typically classified by the kind and content of the elements in the material. Similarly, different contents of elements, such as Mo, Nb, Zr, Si and so on, were usually added into titanium alloys simultaneously to improve the long time performance at elevated temperature. For this case, it is believed that adding multiple alloying elements is a prospective method to improve the properties of Ti<sub>2</sub>AlNb alloy. In this paper, 9 kinds of Ti<sub>2</sub>AlNb alloys with different content of Mo, V and Zr are

melted. The effect of these elements on the microstructure and micro-hardness are detected and discussed. Besides, the microsegregation in different phases was also analyzed.

## 2. Experiment

According to the Mo equilibrium and orthogonal method, 9 kinds of ingots with different compositions were designed based on Ti-22Al-25Nb alloy (at.%). The detailed nominal compositions of the ingots are listed in Table 1. Small button ingots with approximate 160g were melted by vacuum non-consumable arc furnace. To assure the homogeneity, each ingot was melted 5 times at least. The purity of raw materials used in this study were pure Ti, pure Al, pure Zr, AlMo, AlV and NbTi master alloy, respectively.

Table 1 Nominal composition of different button ingots

Sample	Composition (at. %)					
	Ti	Al	Nb	Mo	V	Zr
1#	51.8	23.3	25.2	0.0	0.0	0.0
2#	58.1	22.8	20.5	1.0	1.0	0.0
3#	64.3	22.4	15.9	2.0	2.0	0.0
4#	59.9	22.4	18.5	2.0	0.0	1.0
5#	51.8	23.3	24.0	0.0	1.0	1.0
6#	58.3	22.8	19.1	1.0	2.0	1.0
7#	53.9	22.8	21.7	1.0	0.0	2.0
8#	60.0	22.4	17.1	2.0	1.0	2.0
9#	51.8	23.3	22.6	0.0	2.0	2.0

Samples with 8 mm × 8 mm × 10 mm were cut from the ingot by electro-discharge machining. Subsequently, these samples were heated to single  $\beta$  phase region, held on 1 hour, and then cooled to room temperature in furnace. To study the effect of elements on the microstructures and micro-hardness, all the samples before and after heat treatment were analyzed. For micrograph, the samples were longitudinally sectioned, mechanically polished using standard metallographic techniques and then etched with a solution of 1 ml HF, 3 ml HNO<sub>3</sub> and 5 ml H<sub>2</sub>O.

Leica DM4000M optical microscope and JSM-6460 were used to observe the microstructures of these samples. The chemical composition was analyzed by an energy dispersive X-ray spectroscopy (EDS) detector. Micro-hardness was detected by a Vickers hardness tester. For the measuring accuracy, each sample was detected 5 times at least.

## 3. Results and discussion

### 3.1 Microstructures of different ingots

The typical button ingots prepared by vacuum non-consumable arc furnace are shown in Fig. 1. The ingot has no obvious oxidation and the surface of the ingot is glossy. Columnar grains, which grown directionally from the edge to the inner of the ingot, can be obviously observed.

Fig. 2 shows the microstructures of the as-cast ingots. The grain boundary is clearly observed in these ingots. With the increase of Mo and V, the grain boundary became wider and the precipitations within the grains increased, as shown in 1#, 2# and 3# samples. When the content of Zr is increased up to 2%, it is found that rod-like phase formed within the grains, as shown in 8# and 9# samples. However, for the 4# and 6# samples, although the Mo and V are up to 2%, few precipitations can be observed within most of the grains. Besides, no more regularity was found among these 9 samples before heat treatment and it is confusing that the effect of composition on the microstructure.

According to phase diagram, although the phase transformation is complicated in the range of 960~1060 °C, the solidification path is simple phase transformation from liquid phase to  $\beta$  phase. Thus, only  $\beta$  grains were formed during the solidification. After subsequent cooling procedure, although complicated phase transformation path is inclined undergone, most of the precipitation was restricted due to the high cooling rate and then only a small quantity of precipitations could be observed within those  $\beta$  grains. Besides, because the cooling rate is uncontrollable during the melting process, the cooling rate is inconsistent and thus no obvious regularity with regard to the volume ratio and morphology could be found in these ingots.

### 3.2 Microstructures after heat treatment

In order to investigate the effect of elements on the microstructure and microsegregation of Ti<sub>2</sub>AlNb alloy, all the samples were heated to single  $\beta$  phase region, held on 1 hour, and then cooled to room temperature in furnace. Due to the cooling rate is sufficient low, the  $\alpha_2$  phase and O phase have enough time to form from the  $\beta$ /B2 grains. Fig. 3 shows the microstructures after heat treatment. Different from those microstructures shown in Fig. 2, various morphologies and volumes of equiaxed  $\alpha_2$ /O phase, coarse  $\alpha_2$ /O lath, fine O lamellae and residual  $\beta$ /B2 phase were observed after heat treatment. Within these pictures, the black phase is  $\alpha_2$  phase, the white phase is  $\beta$ /B2 phase and the gray phase is O phase.

When the content of Mo is increased from 0% (1#, 5# and 9#) to 2% (3#, 4# and 8#), the volume of  $\beta$ /B2 phase obviously increases and the fine O lamellae participated from the  $\beta$ /B2 decrease. Besides the primary coarse  $\alpha_2$  lath, a great deal of  $\alpha_2$  phase with tetragon morphology is also observed, which suggests that the orientation relationship between  $\alpha_2$  and  $\beta$ /B2 phase may change with vary of Mo. When the content of V is increased from 0% (1#, 4# and 7#) to 2% (3#, 6# and 9#), the volume of  $\beta$ /B2 phase also increases and the morphology of  $\alpha_2$  phase transforms from coarse lath to tetragon largely. Moreover, it is found that more  $\beta$ /B2 phase is reserved with increasing Mo whereas the amount of tetragon  $\alpha_2$  increases with increasing V. Different from the effects of Mo and V, the volume of  $\beta$ /B2 and  $\alpha_2$  phase decreases obviously when the content of Zr is increased from 0% (1#, 2#, 3#) to 2% (7#, 8#, 9#). Besides, it is also found that the O phase between the  $\beta$ /B2 and  $\alpha_2$  phase increases correspondingly, which suggested that the increasing of Zr can improve the phase transformation of  $\beta$ /B2 +  $\alpha_2$  → O.

Fig. 3(a-c) show the microstructures that Mo and V increase from 0 to 2% simultaneously, the volume of  $\beta$ /B2 phase is increased obviously. Besides, the length of coarse  $\alpha_2$ /O lath and the volume of O phase decrease obviously. When Mo and V is increased up to 2%, most of O phase disappears and the microstructure only consists of  $\beta$ /B2 and  $\alpha_2$  phases, as shown in Fig. 3(c). Besides, numerous primary tetragon  $\alpha_2$  phase is formed from the original  $\beta$  grains. Fig. 3(a, e, i) show the microstructures that V and Zr increase from 0 to 2% simultaneously, the volume of  $\beta$ /B2 and O phase increases whereas the  $\alpha_2$  phase decreases obviously. Simultaneously, it is also found that volume and length of coarse lath also increase. By contrast, with the decrease of Mo and increase of Zr, the  $\beta$ /B2 decreases and the volume and length of lath O phase increase, as shown in Fig. 3 c, f and i.

As discussed above, it is believed that Mo and V are beneficial to the reserve of  $\beta$ /B2 phase and the precipitation of fine O phase is restricted largely correspondingly. Besides, the orientation relationship between the  $\beta$ /B2 and  $\alpha_2$  phase is also changed with the increase of Mo and V. By contrast, with the increase of Zr, both the primary and second  $\alpha_2$  lath becomes more coarse and longer, and the volume of O phase around the  $\alpha_2$  lath increases largely. For this case, only little  $\beta$ /B2 phase can be reserved after the heat treatment.

### 3.4 Composition of different phases

The composition of different phases within the samples is analyzed by EDS. Fig. 4 shows the results of lineal analyze within sample 3 and 5. It is found that the Ti and Al are enriched in  $\alpha_2$  phase and poor in  $\beta$ /B2 phase. By contrast, Nb, Mo and V are enriched in  $\beta$ /B2 phase and poor in  $\alpha_2$  phase. The rim O phase is formed between  $\beta$ /B2 and  $\alpha_2$  phase and then has the transition content between  $\beta$ /B2 and  $\alpha_2$  phase. As is well-known, increasing Al will improve the formation of  $\alpha_2$  phase, whereas Nb, Mo, V is beneficial to increase the ratio of residual  $\beta$ /B2 phase.

The content in different phases of the typical samples is listed in Table 2. The microsegregation in different phases is different with the change of alloy composition. While in 1 # sample, the content of Nb in  $\beta$ /B2 phase is 46% higher than  $\alpha_2$  phase. While in 3# sample, the content of Nb in  $\beta$ /B2 phase is only 28% higher than  $\alpha$  phase. Similarly, the content of Mo and V of  $\beta$ /B2 phase is also higher than that of  $\alpha_2$  phase, and it is found that the microsegregation between  $\beta$ /B2 and  $\alpha_2$  phase increases with the increase of residual  $\beta$ /B2 phase, such as 4#, 6# and 8# sample.

Table 2 Composition of  $\beta$ /B2,  $\alpha$  and O in sample 1#, 3#, 4#, 6#, 8# and 9#.

		Al	Ti	V	Zr	Nb	Mo
Sample 1	$\alpha$	10.35	55.32	/	/	34.34	/
	B2	8.26	41.44	/	/	50.30	/
	O	10.57	45.27	/	/	44.16	/
Sample 3	$\alpha$	10.67	58.52	1.25	/	26.33	3.25
	B2	6.81	51.44	2.72	/	33.71	5.31
	O	8.97	55.84	1.7	/	29.42	4.08
Sample 4	$\alpha$	12.38	63.79	/	0.09	22.59	1.15
	B2	8.5	51.57	/	-0.21	35.68	4.48
	O	8.67	52.7	/	-0.21	34.96	3.88
Sample 6	$\alpha$	12.92	63.01	0.92	0.05	23	0.11
	B2	6.83	47.86	2.13	-1.15	42.47	1.87
	O	8.69	48.68	2.01	-0.62	39.66	1.6
Sample 8	$\alpha$	11.71	62.43	0.3	1.36	23.33	0.9
	B2	9.23	49.31	1.05	1.48	34.24	4.7
	O	10.26	53.97	0.89	0.97	30.57	3.36
Sample 9	$\alpha$	12.67	58.89	0.76	0.81	26.89	/
	B2	6.01	40.76	3.4	1.98	47.85	/
	O	10.36	46.63	1.55	0.37	41.11	/

Note that, when the nominal composition of Zr is lower than 1%, it is difficult to detect the content of Zr in different phases due to the detection precision of EDS equipment. Nevertheless, the microsegregation of Zr in different phases can still be analyzed qualitative. While in 4# and 6# samples, the  $\alpha_2$  phase has more Zr than  $\beta$ /B2 phase. By contrast, while in 8# and 9# samples, the  $\beta$ /B2 phase has more Zr than  $\alpha_2$  phase. What's more, the Zr in O phase is higher than both of  $\alpha_2$  and  $\beta$ /B2 phase, which is somewhat different the other elements.

### 3.4 Micro-hardness

The images in Fig. 6 depict the micro-hardness of different samples before and after heat treatment. Obvious regularity can be observed although little participation is found within most of the samples. With the increase of Zr from 0% to 2%, the mean micro-hardness of the samples increases from 335 to 355. Similarly, the mean micro-hardness slightly increases from 346 to 348 with the increase of Mo. This suggests that the solid solution strengthening of Zr within  $\beta$ /B2

phase is higher than Mo. Different from Mo and Zr, however, the mean micro-hardness decreases obviously with the increase of V. For this case, it is believed that the micro-hardness is depended on the solid solution strengthening. Thus, the micro-hardness of Ti<sub>2</sub>AlNb alloy increases with the increase of Mo and Zr, whereas decreases with the increase of V.

After heat treatment, the micro-hardness of all these samples decreases obviously. As shown in Fig. 2 and Fig. 3, various morphologies and volumes of equiaxed  $\alpha_2/O$ , lath  $\alpha_2/O$  and lamellar O phase were formed after the heat treatment. For this case, the effect of solid solution strength on the micro-hardness decreases whereas the effect of precipitation strength becomes more significant. Therefore, it is suggested that the solid solution strength has more effect on the micro-hardness of Ti<sub>2</sub>AlNb alloy than the solid solution strength.

Nevertheless, it is still found that the effect of element content on the micro-hardness is same to that before heat treatment. With the increase of Mo and Zr and decrease of V, the micro-hardness increase correspondingly, and vice versa. Somewhat differently, the trend of decrease or increase becomes more pronounced after heat treatment, which suggests that the precipitation of different phases enhances the effect of alloy on the micro-hardness of Ti<sub>2</sub>AlNb alloy.

#### 4. Conclusions

1) The microstructure and composition of different phases of Ti<sub>2</sub>AlNb samples after heat treatment are different and are largely dependent on the alloy compositions. The morphology of  $\alpha_2$  phase changed from lamellar to quadrilateral with increasing V and the lath O increased with increasing Zr. Besides, the residual  $\beta/B2$  phase increased with increasing Mo and V. Besides, it is suggested that that Al and Zr were enriched in  $\alpha$  phase whereas Nb, Mo and V were enriched in  $\beta/B2$  phase.

2) The micro-hardness of these samples before and after heat treatment increased with increasing Zr and decreasing Mo and V. And it is suggested that the micro-hardness after heat treatment is lower than that before heat treatment.

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## **Caption of Figures**

Fig. 1 Button ingot obtained by non-consumable arc furnace.

Fig. 2 Microstructure of 1#-9# (a-i) samples before heat treatment.

Fig. 3 Microstructure of 1#-9# (a-i) samples after heat treatment.

Fig. 4 Results of lineal analyze within sample 3#(a) and 5#(b).

Fig. 5 Micro-hardness of different samples before and after heat treatment with different content of Mo(a), V(b), and Zr (c).