Rare Metal Materials and Engineering
Volume 49, Issue 2, February 2020
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Rare Metal Materials and Engineering, 2020, 49(2): 0398-0403.

ARTICLE

Effect of Reinforcement Contents on Microstructure and Mechanical Properties of In-situ Synthesized Ti Matrix Composite

Sun Shuyu[1], Lv Weijie[2]

[1] Taizhou University, Taizhou 318000, China; [2] State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China

Abstract: Four different kinds of TC18 Ti matrix composites containing trace amounts of TiB and TiC were fabricated by in-situ synthesis method. Results show that the merging of β grain is accelerated with increasing the reinforcements during heat treatment, and the standard deviations of β grain size distribution tend to decrease. The microstructure phenomenon is associated with the influence of the reinforcements on the boundary migration of β grains. The pinning ability of the reinforcements to the grain boundary migration decreases, which plays the most important role in the microstructure refinement. The plasticity of the composites is excellent during tensile test. However, when the molar ratio of TiB to TiC in the composites is 4:1, the yield ratios of the composites are all higher than 0.96, and gradually increase with the increase of the reinforcements. The grain boundaries absorb the dislocations, which slows down the increase of dislocation strengthening during the strengthening process. It is suggested that the reinforcements accelerate the absorption of dislocations, and thus lead to this result. The contribution of the microstructure refinement to the toughness increases with the increase of reinforcements.

Key words: TC18 Ti matrix composite; Zener dragging force; microstructure refinement law; yield ratio

TC18 (Ti-5Al-5Mo-5V-Fe-Cr) titanium alloy has become an important aviation structural material due to its good strength and plasticity. The good mechanical properties are ascribed to the unique microstructure characteristics of the material[1-4]. For instance, it presents a spheroidization tendency of primary α grains during heat treatment. Nevertheless, local large deformation zone is likely to appear in the alloy during hot deformation, which cannot be overcome by thermo-mechanical processing and heat treatment[5]. Fortunately, the experiment shows that trace reinforcements can easily remove the defects by accelerating the recrystallization during hot deformation[6].

Conventional Ti alloys modified with discontinuous reinforcements have been widely used in recent years[7,8]. The reinforcements can significantly refine the microstructure. Furthermore, the application of the hybrid reinforcements can achieve better results in improving mechanical properties[9,10].

The length scale for grain size in Ti alloys is an important issue. However, earlier published works do not provide a comprehensive study in microstructure refinement change caused by the change of the hybrid reinforcement content.

Trace reinforcements can remove serious macro segregation of TC18 Ti alloy and accelerate the spheroidization of α during hot deformation. However, the reinforcements have no obvious influence on the spheroidization of α during heat treatment.

Four different kinds of TC18 Ti matrix composites (TMCs) containing trace reinforcements were fabricated by in-situ synthesis method. With the increase of the reinforcements, the merging of β grains is accelerated during heat treatment, and the size distribution of β grains becomes narrower. Considering the particularity of the microstructure, this research

Received date: February 13, 2019
Foundation item: Taizhou Science and Technology Project (1702gy07)
Corresponding author: Sun Shuyu, Ph. D., School of Pharmaceutical and Materials Engineering, Taizhou University, Taizhou 318000, P. R. China, Tel: 0086-576-88660358, E-mail: sun_shuyu@126.com

aims to reveal which factor plays the most important role in the phenomenon.

TC18 TMCs, in which the molar ratio of TiB to TiC is 4:1, have good strength and plasticity after heat treatment. Nevertheless, the values of the yield ratio (yield stress/ ultimate stress) of the composites are very high, which are all above 0.96. Furthermore, the yield ratio tends to increase with increasing the reinforcements. Little information is available to date on the influence of the reinforcement contents on the yield ratios of TC18 TMCs. Therefore, this work also focuses on the variation tendency of yield ratio.

1 Experiment

The stoichiometric mass fractions of the raw materials including sponge Ti, B_4C powder, Al, Al-Mo, Al-V, Fe and Cr were uniformly blended, and they were compacted into pellets. The pellets were melted in a consumable vacuum arc-remelting furnace. The melting was repeated two times to improve the microstructure uniformity.

Small addition of B_4C to Ti produces TiB and TiC during solidification by a chemical reaction: $5Ti + B_4C = 4TiB + TiC$. The addition contents of B_4C were 0.1 wt%, 0.2 wt% and 0.4 wt%, referred to as TMC1, TMC2 and TMC3, respectively. The molar ratio of TiB to TiC in TMCs was 4:1. Additionally, another kind of composite called TMC4 was fabricated. The volume fraction of the reinforcements in TMC4 was the same as that in TMC1. However, the molar ratio of TiB to TiC reaches 1:1. By calculation, the addition content of B_4C was 0.06 wt%. Moreover, a small amount of C powder (0.04 wt%) was also added in the raw materials. C and Ti produce TiC by chemical reaction: Ti+C=TiC.

The as-cast ingots were then forged at 1150 °C and rolled at 840 °C into rods with the diameter of 15 mm. Phase identification indicates that there are three kinds of phases in the composites, Ti, TiB and TiC. In order to control the overgrowth of grains and obtain good mechanical properties, triplex heat treatment procedures were as follows:

(1) Heat treatment A (HTA): 830 °C/1.5 h+furnace cooling, 750 °C/1.5 h+air cooling, 600 °C/4 h+air cooling.

(2) Heat treatment B (HTB): 860 °C/1.5 h+furnace cooling, 750 °C/1.5 h+air cooling, 600 °C/4 h+air cooling.

Anti-oxidation coating was used during heat treatment. The alloy was also prepared by the same method.

For tensile testing, 30 mm gage length cylindrical specimens (6 mm in diameter) were machined from the rods undergone HTA treatment. Tensile tests were carried out in a servohydraulic testing machine with a strain rate of 0.001 s^{-1}. The deformation within gage length of tensile specimen was measured by vernier caliper.

Microstructure observation was conducted by optical microscope (OM) and scanning electron microscope (SEM) after polishing and etching with reagent. The volume fractions of HF, HNO_3 and H_2O in the reagent were 30 vol%, 10 vol% and 60 vol%, respectively.

OM and SEM samples were extracted via electric discharge machining from the clamping parts of the tensile specimens. Optical micrographs at magnifications from 100× to 500× were used to calculate grain sizes by the linear intercept method. Moreover, transmission electron microscope (TEM) was also used. TEM samples were made by electro polisher. The microstructure observations were conducted at room temperature.

2 Results and Discussion

2.1 Microstructure characteristics of as-cast materials

Fig.1a shows the microstructure of as-cast alloy. The phase contrast of α is black. Owing to the high contents of β stabilizing elements (Mo, V, Fe and Cr), α grain shows a needle-shaped morphology. According to the composition, the molybdenum equivalent ([Mo]eq) of TC18 Ti alloy in this research is 12. When [Mo]eq is about 10, the strength of Ti alloy can be maximized[11].

The stabilizing effect of Fe and Cr on β phase is much higher than that of Mo and V. Nevertheless, Fe often causes the segregation of the alloying elements during solidification. Cr can hinder the recrystallization during hot working and aggravate the segregation. Therefore, the as-cast microstructures and the microstructures after the thermo-mechanical processing exhibit inhomogeneity.

TiB short fibers can act as nucleation site for the precipitation of α during solidification, as shown in Fig.1b. The

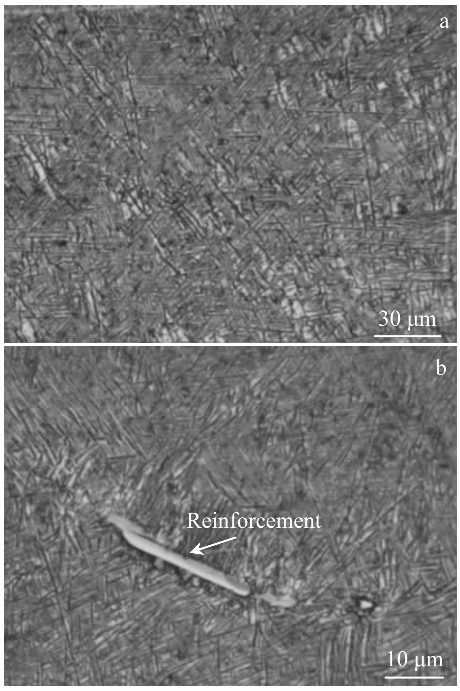

Fig.1 OM images of as-cast alloy (a) and as-cast TMC3 (b)

in-situ synthesized TiB and TiC have small length scale since the mass fractions of B_4C or C powder are very small. The solid solubility of B and C is very low in Ti alloy, e.g., the solubility of B is less than 0.02 wt%. Solute enrichment results in constitutional supercooling, which in turn provides the driving force for nucleation and increases the nucleation rate. Further- more, excess B and C in the solid-liquid interface also decrease the growth rate of the grains. Therefore, β grains are refined during solidification[12].

2.2 Microstructure refinement during heat treatment

Owing to the effect of anti-oxidation coating, β phase boundary decorated with α can be observed after HTB treatment. TiB and TiC have significant influence on β grain growth. The average sizes of β grains in the alloy, TMC1, TMC2, TMC3 and TMC4 are about 38.3, 22.6, 17, 15.8 and 20.5 μm, respectively. The standard deviations of β grain size distributions are about 16.3, 6.9, 4.1, 2.9 and 6.8 μm, respectively. With the increase of the reinforcements, the grain size distribution becomes narrower, and thus the topological defects of β grains decrease.

Fig.2 shows the reinforcements in TMC3 after HTB treat- ment. The stacking faults of TiB can be observed in Fig.2a, which can decrease the mismatch. In Fig.2b, the different thermal expansion coefficients of TiC and the matrix cause dislocation multiplication during heat treatment. TiB and TiC

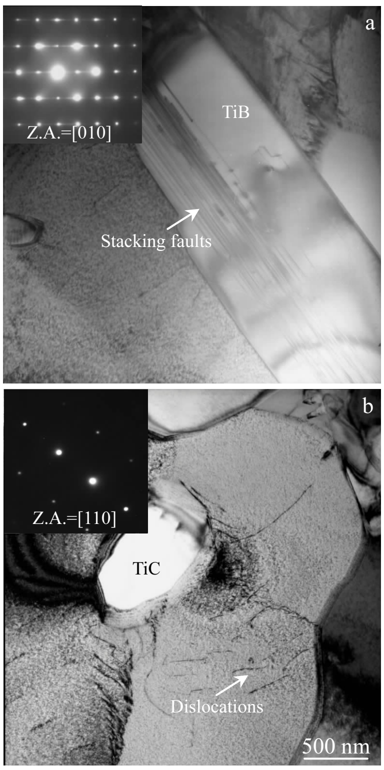

Fig.2 TEM images and corresponding SAED pattern of reinforce- ments in TMC3: (a) TiB and (b) TiC

have an average length of about 7.9 and 2.6 μm, respectively. Since B_4C or C power in the raw materials is very small, there is almost no size difference among the reinforcements in the materials.

TiC in this research has a wide range of size distribution, from less than 200 nm to more than 4 μm. A broad size distribution of particles is favorable for achieving large Zener dragging force[13].

Three kinds of TMCs, in which the molar ratio of TiB to TiC is 4:1, were compared. The variation of average sizes of β grains in the composites is associated with Zener dragging force exerted by the reinforcements[14]. With the increase of the reinforcements, the decrease of topological defects leads to the decrease of grain boundary energy. Zener dragging force is directly proportional to average grain boundary energy. Therefore, the pinning capability of the reinforcements to the boundary migration of β grains tends to decrease. Furthermore, the average rate of grain boundary migration increases, which not only means the decrease in Zener dragging force , but also depends on the increase of driving force for grain boundary migration.

TiB short fibers cause anisotropy during the boundary migration of β grains. TiC particles can exert relatively large Zener dragging force due to small size. The standard deviation of β grain size in TMC4 is nearly the same as that in TMC1. However, larger volume fraction of TiC in TMC4 can exert larger Zener dragging force. Moreover, because of larger distortion energy, short fibers in TMC1 result in greater driving force for the grain boundary migration. Nevertheless, the average β grain size of TMC1 is higher than that of TMC4. Therefore, comparing TMC1 with TMC4, the effect of Zener dragging force exerted by the reinforcements on β grain refinement is stronger.

The reinforcements increase the distortion energy diffe- rence between adjacent β grains, which increases the driving force for the boundary migration of β grains. Nevertheless, the in-situ synthesized reinforcements are relatively uniformly distributed after heat treatment. Therefore, the increase of the driving force caused by the increase of the distortion energy difference between adjacent β grains is restricted.

The topological defect provides extra driving force for grain boundary migration. However, the improvement of the microstructure homogeneity indicates that the increase of the topological defects gradually drops with the increase of the reinforcements. Therefore, the increase of the driving force provided by the topological defect is also restricted.

Moreover, the acceleration of the diffusion can also accelerate the boundary migration of β grains. Nevertheless, the increase of the segregation caused by the reinforcements decreases the effect of the diffusion.

In summary, the increase of the driving force for the boundary migration of β grains does not play the most important role in the microstructure refinement.

Fig.3 shows the annealing twins in α in TMC3 after HTB treatment. The interfacial energy of the annealing twins is stacking fault energy. There is only in-situ recrystallization in α due to the high stacking fault energy of hcp structure and the dispersion of α. The spheroidization of α is determined by the degree of the recrystallization during heat treatment. The influence of the trace reinforcements on the recrystallization of α is a competitive result between accelerating the diffusion and increasing the segregation. However, the positive effect and the negative effect of the reinforcements on the spheroidization of α almost reach a dynamic balance[14]. In addition, topological defects are gradually decreased. Therefore, the pinning effect of grain boundary segregation caused by the reinforcements cannot play an obvious role in the microstructure refinement. The variation of Zener dragging force of trace reinforcements is the primary reason for the grain refinement.

2.3 Yield ratio of the composites

The composites have good strength and plasticity. The yield stress σ_y, the ultimate stress σ_b, the elongation δ, the reduction of area ψ, and the yield ratio are provided in Table 1. With the increase of the reinforcements, the plasticity tends to decrease, and the yield ratio tends to increase.

Fig.4 presents the microstructure characteristics of TMC3 specimen during the strengthening process. Some α and β grains are not obviously elongated. Most TiB short fibers tend to be parallel to the external force, indicating that TiB short fibers bear most of the load. However, it is also observed that some short fibers are not parallel to the external load but distributed along β grain boundary, which means that grain boundary sliding also accounts for a certain proportion in the total deformation.

The promotion of the strength of TMC is contributed to the load-bearing of TiB, dispersion strengthening of TiC and grain refinement strengthening[12,15,16]. The critical aspect ratios of TiB of the composites are 1.73, 1.63 and 1.54, according to Kelly formula. Nevertheless, the average aspect ratio of TiB is 7.1, which is significantly higher than the critical aspect ratios. Furthermore, TiB tends to be parallel to the external force during the tensile test, which further promotes the load-bearing.

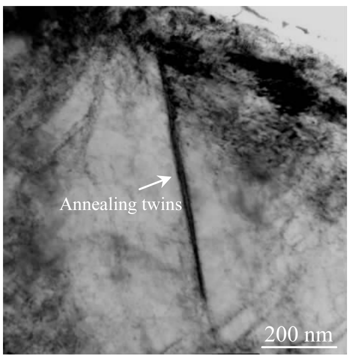

Fig.3 TEM image of annealing twins in α in TMC3 after HTB treatment

Table 1 Tensile properties of TMCs after HTA treatment

Specimen	σ_y/MPa	σ_b/MPa	δ/%	ψ/%	σ_y/σ_b
TMC1	1010.25	1050.29	21.55	63.9	0.962
TMC2	1074.33	1104	16.75	51.05	0.973
TMC3	1136.36	1167.2	14.65	41.46	0.974

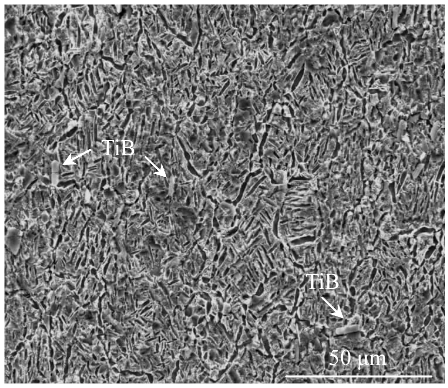

Fig.4 SEM image of the longitudinal section of TMC3 tensile specimen

According to the microstructure refinement law and Hall-Petch formula, the increase of the grain refinement strengthening gradually drops.

The mechanism of grain refinement strengthening is to increase the dislocation piling-up by increasing the interfaces, and thus dislocation strengthening is increased. However, when the dislocations enter the grain boundaries, the increase of the dislocation strengthening slows down during the strengthening process of tensile test, which causes high value of yield ratio[6]. The absorption of dislocations by the grain boundaries not only decreases dislocation piling-up, but also is beneficial to grain boundary sliding, thus increasing the proportion of grain boundary sliding in the total deformation of β grains. The improvement of the microstructure homogeneity decreases the topological defects of β grains, which is also beneficial to grain boundary sliding. Therefore, the refinement of β grains can help to improve the plasticity of TC18 TMC during tensile test.

The increase of the yield ratio with the increase of the reinforcements is associated with dislocation motion. The reinforcements increase the segregation, which has pinning effect on dislocation motion. Meanwhile, the reinforcements accelerate dislocation motion by increasing the distortion energy. More reinforcements cause more dislocation multiplication and piling-up. Furthermore, the increase in the number of β grains slows down with increasing the reinforcements. However, the increase of the dislocation strengthening becomes slower and slower with the increase of the reinforcements. It is suggested that the reinforcements accelerate the absorption of dislocations during the strengthening process of the tensile test.

β grain refinement not only increases the strength but also improves the plasticity of TC18 TMCs. Therefore, grain refinement plays a toughening role. Since the reinforcements promote the absorption of dislocations by grain boundaries, the effect increases with the increase of reinforcement. The toughening effect of grain refinement is enhanced with the increase of the reinforcements.

2.4 Plasticity of the composites

The load bearing effect of TiB short fibers improve the elongation. The effect increases with the increase of TiB. Furthermore, since the reinforcements can accelerate the absorption of dislocations, the contribution of the microstructure refinement to the elongation also increases with the increase of reinforcements. However, more reinforcements also result in more crack nucleation, which decreases the elongation. Therefore, the elongation tends to decrease finally, as shown in Table 1.

Since most reinforcements fail at the necking area of the tensile specimen, the reduction of area is mainly associated with the microstructure refinement. With the increase of the reinforcements, the decrease of topological defects, as well as the enhancement of dislocation absorption by grain boundaries are both beneficial to grain boundary sliding. In addition to the effect of grain interfacial strength, the increase of the proportion of grain boundary sliding in the total deformation of β grains can help to improve the reduction of area.

Fig.5 shows fractographs of TMC1. The macroscopic fracture surface in Fig.5a only includes the shear lip and the fiber area, and there is no radiation area, which indicates that the plasticity of the material is very good. The tearing at the bottom of the dimple is the crack source, as shown in Fig.5b. Fractured TiB fiber in Fig.5c causes crack nucleation. Fig.5d shows the crack deflection during the crack propagation.

The hardness of α with hcp structure is higher than that of β with bcc structure. When the aspect ratio of elongated primary α is higher than the critical aspect ratio, the elongated α grains are loaded along α/β interfaces. The load-bearing of primary α can also help to promote the reduction of area.

The spheroidization of α can reduce dislocation multiplication and piling-up, and thus reduce the crack nucleation. The transgranular fracture of the elongated α can consume a large number of energy of crack propagation, which further improves the reduction of area.

Since the energy of crack propagation increases, the changes in the morphology of the crack tip, such as blunt, bifurcation, as well as crack deflection resulted from the reinforcements also help to improve the plasticity[17,18]. However, partial increase of the plasticity is offset by the negative effect of the reinforcement. The broken and deboned reinforcements accelerate crack propagation, which leads to the decrease tendency of the reduction of area.

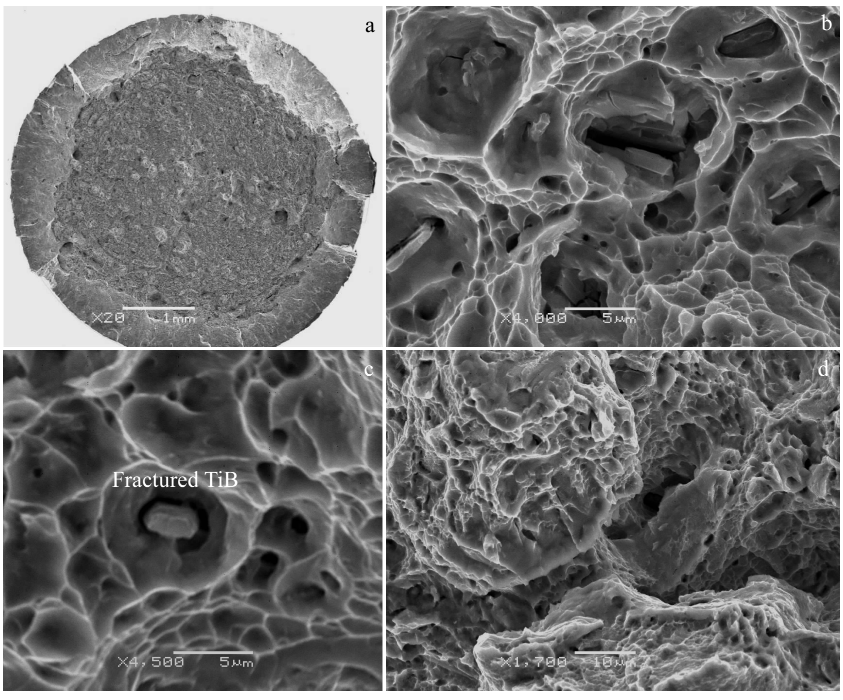

Fig.5 SEM fractographs of TMC1: (a) macroscopic fracture surface, (b) crack source, (c) fractured TiB causing crack nucleation, and (d) crack deflection during crack propagation

3 Conclusions

1) The merging of β grains in TC18 TMCs is accelerated with increasing the reinforcements during heat treatment. The pinning capability of the reinforcements to the boundary migration of β grains gradually decreases, which plays the most important role in the microstructure refinement.

2) β grain refinement of TC18 TMC has toughening effect during room temperature tensile test. When the molar ratio of TiB to TiC in TC18 TMCs is 4:1, since the reinforcements can accelerate the absorption of the dislocations by grain boundaries, the yield ratio tends to increase with increasing the reinforcements. Moreover, the toughening effect of grain refinement is enhanced with the increase of the reinforcements.

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增强体含量对原位合成钛基复合材料微观组织及力学性能的影响

孙曙宇 [1]，吕维洁 [2]

(1. 台州学院，浙江 台州 318000)

(2. 上海交通大学 金属基复合材料国家重点实验室，上海 200240)

摘　要：使用原位自生法制备出 4 种 TC18 钛基复合材料。结果表明，热处理过程中随着增强体含量增加，β 晶粒的合并速度加快，且 β 晶粒的尺寸分布标准差呈现下降的趋势，该组织现象与增强体对 β 晶界迁移的影响有关。增强体对晶界迁移钉扎能力的下降是导致该细化规律的首要原因。TiB 和 TiC 摩尔比为 4:1 的复合材料在拉伸试验中塑性俱佳，但是屈强比却均高于 0.96，且随着增强体含量增加呈现增加的趋势。拉伸过程中晶界对位错的吸收致使位错强化增加减缓，增强体加速了晶界对位错的吸收从而导致了上述结果，也正因为如此，晶粒细化对增韧作用的贡献会随着增强体含量增加而增加。

关键词：TC18 钛基复合材料；辛纳拖曳力；组织细化规律；屈强比

作者简介：孙曙宇，男，1971 年生，博士，台州学院医化与材料工程学院，浙江 台州 318000，电话：0576-88660358，E-mail: sun_shuyu@126.com