



Effect of solid carburization on surface microstructure and hardness of Ti–6Al–4V alloy and (TiB+La₂O₃)/Ti–6Al–4V composite

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Abstract: Solid carburization was employed to improve the hardness of Ti–6Al–4V alloy and (TiB+La₂O₃)/Ti composite. The samples wrapped in graphite powder were placed in sealed quartz tubes, followed by solid carburization at 1227 K for 24 h. Microstructure and phase analysis indicated that TiC reinforcements and Ti–C solid solutions were introduced after solid carburization. Moreover, the volume fraction of equiaxed α -Ti phase in diffusion layer decreased obviously with increasing sample depth. Hardness testing results indicated that both the carburized surfaces performed significant improvement of about 100% in micro-hardness compared with untreated materials. The variation of carbon contents with increasing sample depth resulted in a hardened layer of 300 μ m in the carburized samples. Meanwhile, slight influence on the internal microstructure and hardness indicated that solid carburization was an effective method in strengthening the surface of titanium alloy and titanium matrix composite.

Key words: titanium alloy; titanium matrix composite; solid carburization; microstructure; micro-hardness

1 Introduction

Titanium and titanium alloys have been widely used in aerospace, chemical, biomedical industries due to their high specific strength and excellent corrosion resistance and biocompatibility [1]. Ceramic reinforcements with high elastic modulus and high strength are incorporated into titanium alloys to further improve the specific strength and stiffness [2]. Titanium matrix composites (TMCs) perform good combination of excellent mechanical properties and high temperature durability, which render them attractive materials for commercial automotive, aerospace and advanced military applications [3]. In situ synthesized discontinuously reinforced TMCs have drawn considerable interest due to strong interface bonding, good interfacial integrity, and cost-saving fabricating process [4]. The in situ synthesis methods mainly include self-propagation high temperature synthesis (SHS) [5], powder metallurgy (PM) [6], mechanical alloying (MA) [7], rapid solidification process (RSP) [8], ingot metallurgy (IM) [9], etc. However, low fracture ductility of TMCs with

high volume fraction of reinforcements seriously restricts the practical application compared with monolithic titanium and titanium alloys [10,11]. On the contrary, ductile titanium alloys and TMCs with low volume fraction of reinforcements show unsatisfactory wear resistance such as high friction coefficient and low hardness [12,13]. Therefore, lots of surface modification methods have been proposed to strengthen the surface of titanium alloys and titanium matrix composites.

Common surface engineering methods can be divided into three main groups: heat treatment, coatings and thermochemical treatment [14,15]. The most attractive method, thermochemical treatment, includes laser carburizing and nitriding, plasma carburizing, plasma alloying, gas carburizing, gas nitriding and glow discharge methods [16–18]. The diffusion treatment techniques significantly strengthen the surface by introducing a hardened layer, which is composed of solid solutions and ceramic particles due to implantation of carbon and nitrogen into the titanium alloys respectively [17–19]. As discussed in Refs. [20,21], the carburized layer was formed on the surface of Ti–6Al–4V alloy and TiAl alloy by plasma carburizing.

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Significant improvement in surface hardness and wear resistance could be attributed to various carbide particles in the carburized layer. Laser surface alloying [22] and cladding [23] were employed to strengthen the surface of pure Ti and Ti-6Al-4V alloy. Significant increase in hardness and wear resistance was observed compared with untreated materials due to the introduction of TiC phase. WU et al [24] investigated the effects of molten salt carburization parameters on the surface hardness and tribological properties of Ti-6Al-4V alloy. The result indicated that major hardening effect was considered to be the formation of solid solution of carbon in α -Ti. However, the major limitation of above carburizing methods in application is the problem of high cost and complicated equipment. Meanwhile, most previous researches focus on pure titanium and Ti-6Al-4V alloy. Further research of simple carburization technology on TMCs is still required due to their attractive mechanical properties of high specific strength and stiffness.

In this study, solid vacuum carburization on Ti-6Al-4V alloy and (TiB+La₂O₃)/Ti-6Al-4V composite was carried out to improve the surface hardness without affecting the internal microstructure. The (TiB+La₂O₃)/Ti-6Al-4V composite with low volume fraction of reinforcements was selected because TiB was considered to be the best reinforcement and lanthanum element could reduce the oxygen content in the matrix alloy [9]. Graphite powder was employed as carbon supply to avoid hydrogen brittleness. The constituent phases in the carburized layer were determined by X-ray diffraction. Microstructure and micro-hardness were analyzed to evaluate the reaction and diffusion behavior of Ti-6Al-4V alloy and (TiB+La₂O₃)/Ti-6Al-4V composite during solid carburization.

2 Experimental

2.1 Materials

Forged Ti-6Al-4V alloy and (TiB+La₂O₃)/Ti-6Al-4V composite were used as experimental materials. Figure 1 shows the different original microstructures of the two untreated experimental samples. Figure 1(a) shows the uniform duplex microstructure of Ti-6Al-4V alloy, which is composed of equiaxed α phase and lamellar α phase. The size of equiaxed α phase is about 10 μ m, while the thickness of lamellar α phase is only several hundred nanometers. Figure 1(b) shows the microstructure of (TiB+La₂O₃)/Ti-6Al-4V composite. It can be observed that TiB whiskers with the length of 5–10 μ m are distributed homogeneously in the lamellar microstructure matrix alloy.

2.2 Solid carburization

Ti-6Al-4V alloy and (TiB+La₂O₃)/Ti-6Al-4V composite samples with dimensions of 10 mm $\times$ 10 mm $\times$ 3 mm were prepared by wire cutting. The polished samples wrapped in graphite powder were placed in quartz tubes respectively. The quartz tubes were sealed in argon to keep the samples from being oxidized at high temperatures. Solid vacuum carburization was carried out in a box type electric resistance furnace at 1227 K for 24 h. Figure 2 shows the schematic diagram of the solid vacuum carburization process. The carburized samples were taken out after cooling down to room temperature in the heat treatment furnace.

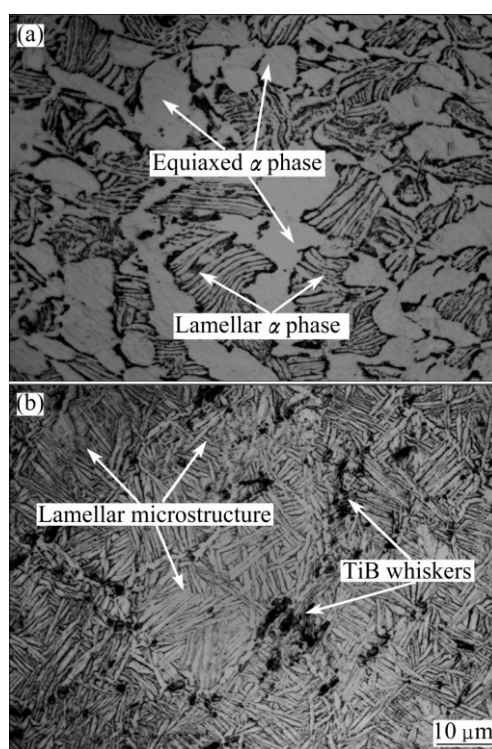


Fig. 1 Original microstructures of experimental samples: (a) Ti-6Al-4V alloy; (b) (TiB+La₂O₃)/Ti-6Al-4V composite

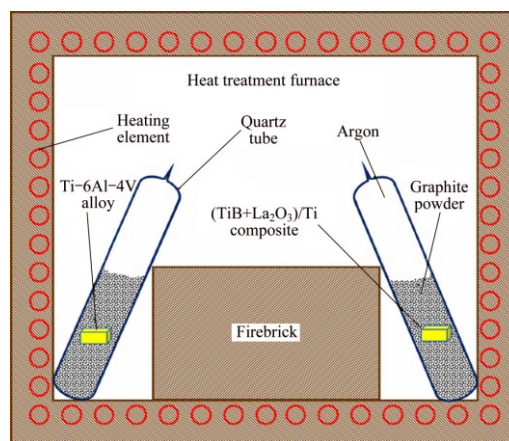


Fig. 2 Schematic diagram of solid vacuum carburization process

2.3 Characterization

The carburized Ti-6Al-4V alloy and (TiB+La₂O₃)/Ti-6Al-4V composite were polished and etched in Kroll reagent. The cross-sectional microstructure was analyzed by optical microscopy (OM), field emission scanning electron microscopy (FEI Quanta 250 FESEM) and electron dispersive spectroscopy (EDS). The constituent phases in the carburized samples were determined by X-ray diffraction (XRD) under the X-ray power of 35 kV and 200 mA with Cu K α radiation. All traces were obtained over a 2θ range from 10° to 90° with a 4 (°)/min scanning speed. The micro-hardness values of the samples were measured using a Knoop micro-hardness tester (402SXV) under a 200 g load for duration of 15 s. At least ten hardness values were measured in each region to get a representative result.

3 Results and discussion

3.1 XRD analysis

Figure 3 shows the XRD patterns of the carburized Ti-6Al-4V alloy and (TiB+La₂O₃)/Ti-6Al-4V composite compared with the untreated samples. As shown in Figs. 3(a) and (c), in addition to the peaks (α -Ti phase and β -Ti phase) of matrix alloy, the peaks of TiC phase appear in both the XRD patterns of carburized

Ti-6Al-4V alloy and (TiB+La₂O₃)/Ti-6Al-4V composite. Furthermore, broad peaks in Figs. 3(a) and (c) indicate that the α -Ti phase may be saturated by carbon atoms [18]. As discussed in Ref. [19], it is easy to form compounds and solid solutions between carbon and titanium due to the small atomic radius (0.091 nm) of carbon, which is far smaller than that of titanium (0.2 nm). The results in Fig. 3 indicate that TiC phase and Ti-C solid solutions are successfully introduced into the surface region after solid carburization due to the reaction and diffusion between active carbon atoms and titanium atoms.

3.2 Microstructure

Figure 4 shows the cross-sectional SEM micrographs of the carburized samples. Figure 4(a) displays the uniform duplex microstructure of carburized Ti-6Al-4V alloy. It can be observed that the size of equiaxed α phase ranges from 10 to 20 μ m, and the thickness of lamellar α phase is about 1 μ m. Figure 4(b) shows that TiB whiskers distribute uniformly in the lamellar structure matrix of carburized (TiB+La₂O₃)/Ti-6Al-4V composite. The results indicate that solid vacuum carburization has very limited influence on the internal microstructure of matrix alloy compared with untreated samples in Fig. 1. Meanwhile, carburized layer

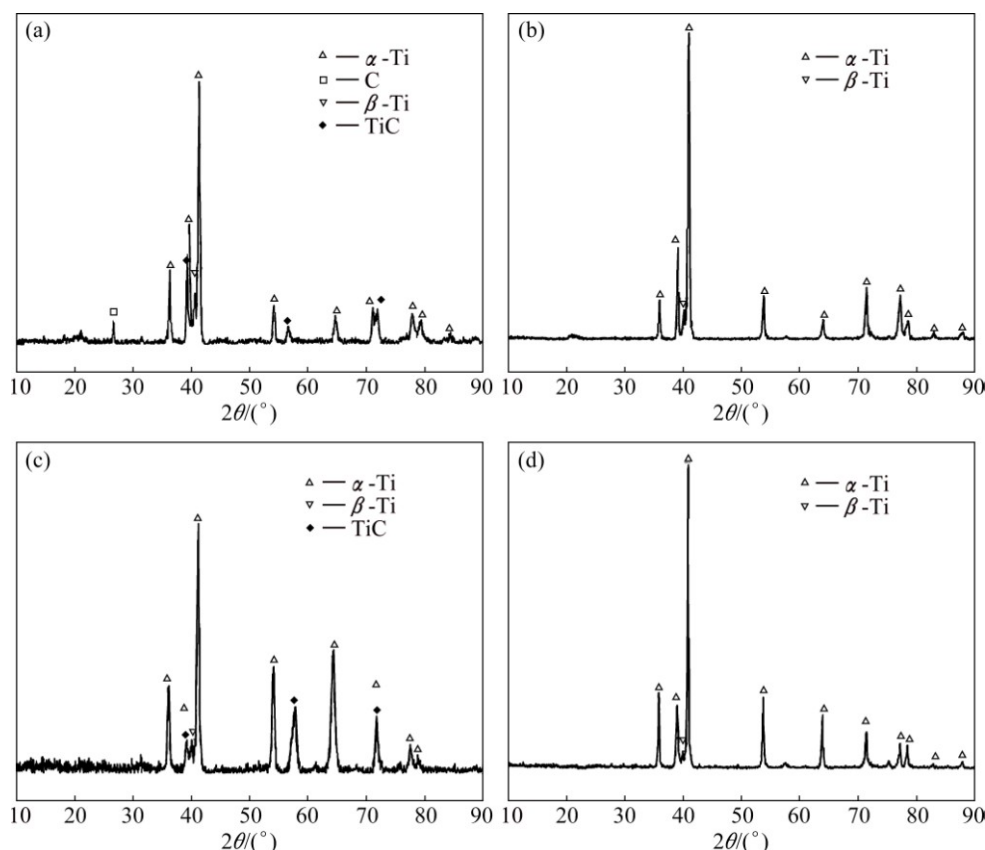


Fig. 3 XRD patterns of carburized Ti-6Al-4V alloy (a), untreated Ti-6Al-4V alloy (b), carburized (TiB+La₂O₃)/Ti-6Al-4V composite (c), and untreated (TiB+La₂O₃)/Ti-6Al-4V composite (d)

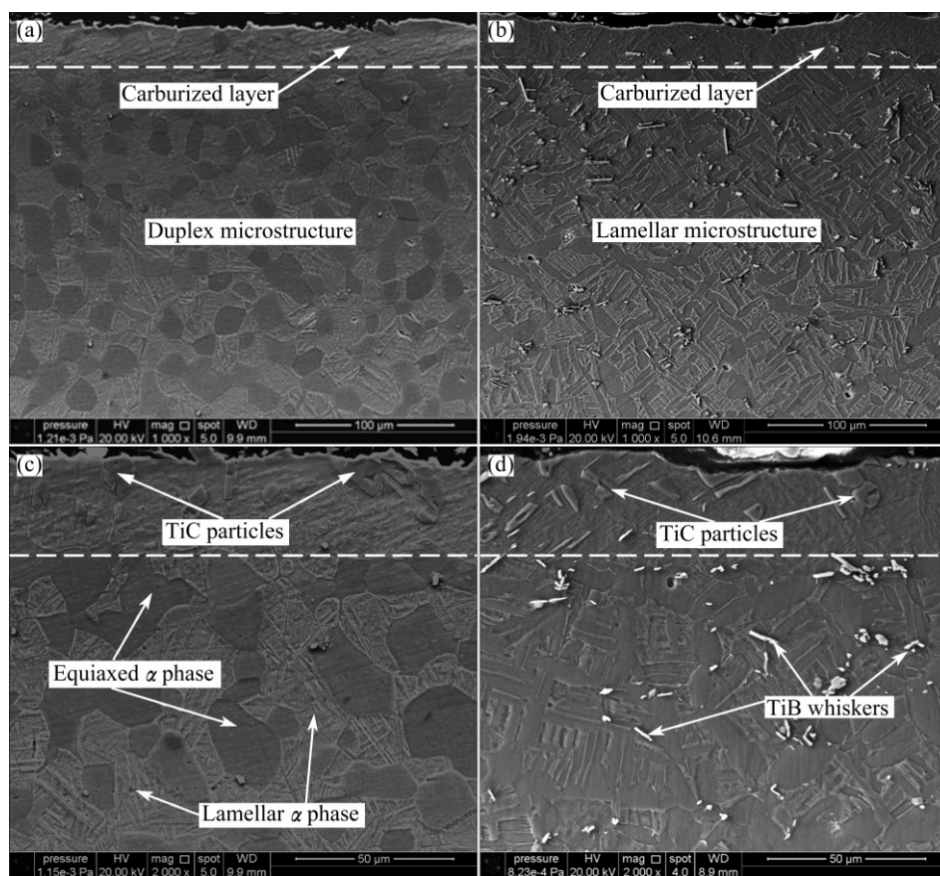


Fig. 4 Cross-sectional microstructures of carburized Ti-6Al-4V alloy (a), carburized (TiB+La₂O₃)/Ti-6Al-4V composite (b), carburized Ti-6Al-4V alloy (c), and carburized (TiB+La₂O₃)/Ti-6Al-4V composite (d)

with the thickness of 30 μm is formed on the surface of both carburized Ti-6Al-4V alloy and (TiB+La₂O₃)/Ti-6Al-4V composite.

As shown in Figs. 4(c) and (d), equiaxed TiC particles can be observed in both the carburized layers of carburized Ti-6Al-4V alloy and (TiB+La₂O₃)/Ti composite. The size of hard TiC particles ranges from 5 to 10 μm . TiC has outstanding chemical stability and compatibilities with the titanium matrix due to the similar density (Ti: 4.51 g/cm³, TiC: 4.91 g/cm³) and analogous coefficient of thermal expansion [25]. Moreover, TiC is widely used in the fields of wear resistance tools and materials due to the attractive and superior mechanical properties. Therefore, it can be considered that hard TiC particles in carburized layer play an important part in strengthening the surface of carburized samples.

3.3 Carbon content

Figure 5(a) shows the cross-sectional microstructure of carburized Ti-6Al-4V alloy at low magnification. It can be seen that a diffusion layer characterized by gradient feature is formed tightly below the carburized layer. Figures 5(b) and (c) show that the size and amount of transferred β microstructure, the mixture of β phase

and second α phase increase with the increase of the sample depth in the diffusion layer. The result can be attributed to the effect of carbon element because carbon is one of the α -stabilizing elements in titanium alloys [26]. Figure 5(d) presents the carbon content of carburized Ti-6Al-4V alloy measured by EDS point analysis at different depths. The mole fraction of carbon decreases gradually from surface to interior, which is consistent with the variation tendency of volume fraction of equiaxed α phase. The carbon content of 65.91% at Position 1, indicates that redundant graphite residues besides TiC particles are formed on the surface after solid carburization. While the carbon contents at Positions 2–5 show that Ti–C solid solutions and a few TiC reinforcements are introduced into the diffusion layer due to the limited solid solubility of carbon in titanium alloys [20].

Figure 6 shows similar results in the carburized (TiB+La₂O₃)/Ti-6Al-4V composite. Figures 6(a)–(c) show that both the size and volume fraction of transferred β microstructure increase with the increase of the sample depth, while the carbon content shows an opposite tendency in Fig. 6(d). Similarly, the carbon content at Position 1, 35.52% indicates that a number of TiC particles are formed in the carburized layer. And the

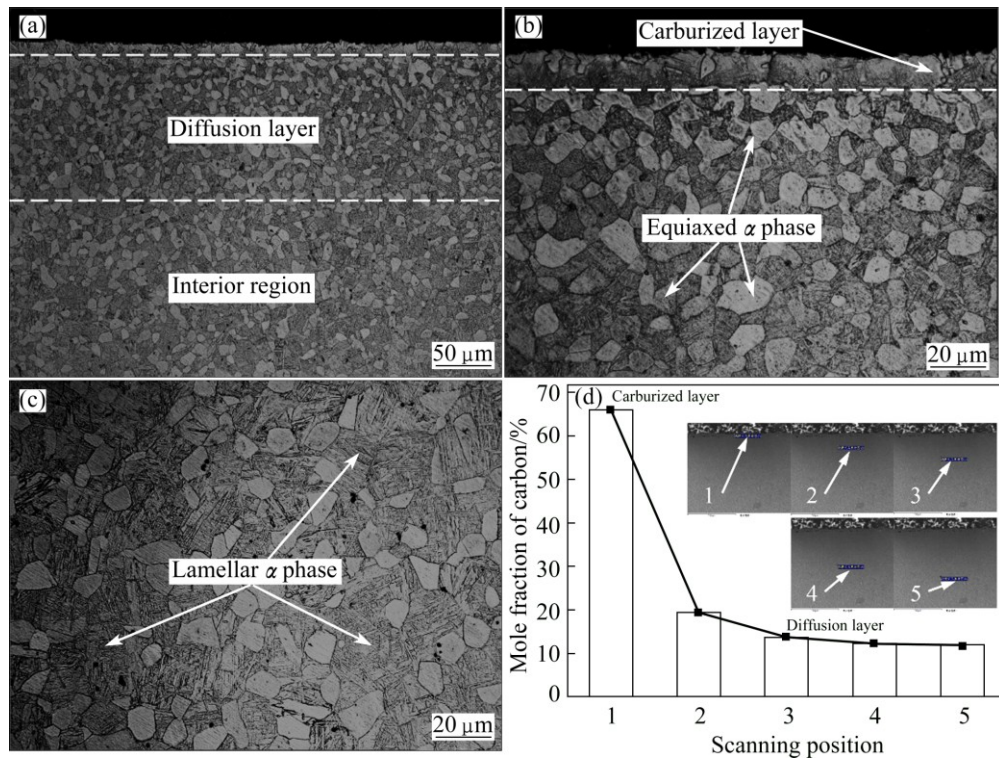


Fig. 5 Microstructures and composition of carburized Ti-6Al-4V alloy: (a) Microstructure at low magnification; (b) Carburized layer and diffusion layer; (c) Internal microstructure; (d) Variation of carbon content

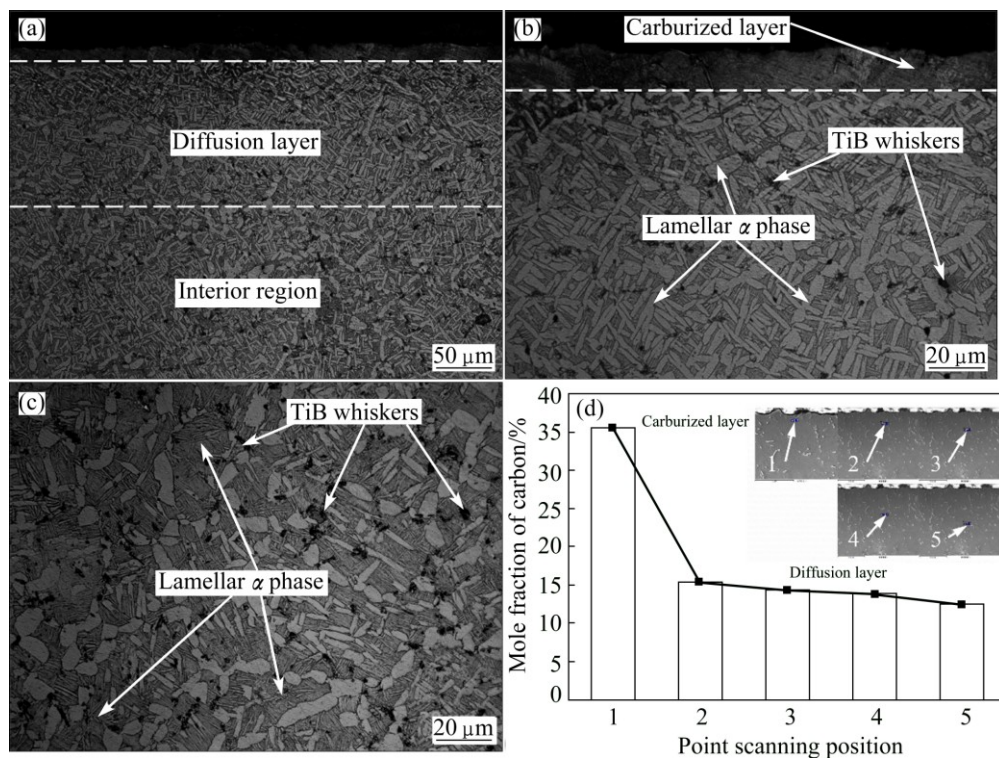


Fig. 6 Microstructure and composition of (TiB+La₂O₃)/Ti-6Al-4V composite: (a) Microstructure at low magnification; (b) Carburized layer and diffusion layer; (c) Internal microstructure; (d) Variation of carbon content

values at Positions 2–5 indicate that Ti–C solid solutions and a few TiC reinforcements are formed in the diffusion layer. Therefore, the results indicate that the reaction and

diffusion between active carbon atoms and titanium atoms are simultaneous during carburizing, which results in the formation of carburized layer and diffusion

layer in the carburized Ti–6Al–4V alloy and (TiB+La₂O₃)/Ti composite.

3.4 Micro-hardness

Hardness is widely considered to be a good method to check the degree of hardening, and the Knoop micro-hardness test results are used to evaluate the mechanical properties of carburized Ti–6Al–4V alloy and (TiB+La₂O₃)/Ti composite. Figure 7 shows the cross-sectional hardness–depth relationship for the carburized samples from surface to interior. It can be seen that both the micro-hardness values of carburized Ti–6Al–4V alloy and (TiB+La₂O₃)/Ti–6Al–4V composite decrease gradually to a stable value of about HK 380 at the depth of 300 μ m. The maximum micro-hardness value is obtained on the carburized surface, which shows an improvement of about 100% to more than HK 700 compared with the internal micro-hardness. Moreover, it can be observed that the hardness values show a dramatic decline at the beginning and then decrease very slowly until stably, which indicates that the hardened layer in both the carburized samples includes a carburized layer about 30 μ m and a diffusion layer more than 200 μ m. The results coincide with the microstructure observation in Fig. 4 and the carbon content analysis in Figs. 5 and 6.

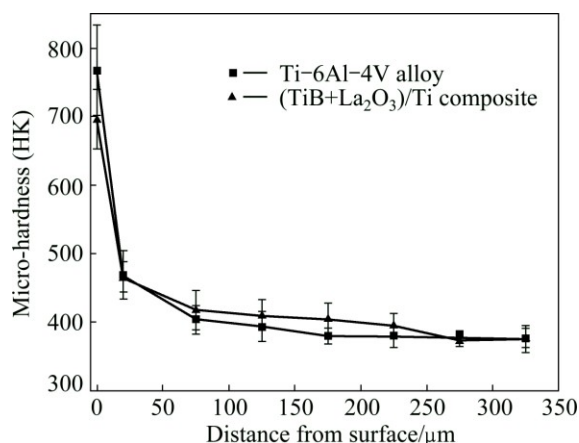


Fig. 7 Hardness–depth relationship between carburized Ti–6Al–4V alloy and (TiB+La₂O₃)/Ti–6Al–4V composite

The micro-hardness value of the untreated Ti–6Al–4V alloy is HK 387, while that of the untreated (TiB+La₂O₃)/Ti–6Al–4V composite is HK 374. It can be seen obviously that solid vacuum carburization can significantly improve the surface hardness of Ti–6Al–4V alloy and (TiB+La₂O₃)/Ti–6Al–4V composite, meanwhile, keep the hardness values of internal matrix alloys. According to Refs. [27,28], the enhancement of hardness can be attributed to the generation of high volume fraction of TiC reinforcements (precipitation hardening effect) and the increase of carbon content in

α -Ti phase (solution hardening effect), which can geometrically increase density of dislocations, decrease grain size and transfer load. Therefore, solid vacuum carburization can be considered as a meaningful method to strengthen the surface of Ti–6Al–4V alloy and (TiB+La₂O₃)/Ti composite.

4 Conclusions

1) A hardened layer, which consists of a hard carburized layer and a diffusion layer with gradient feature, is formed on both Ti–6Al–4V alloy and (TiB+La₂O₃)/Ti composite after solid carburization.

2) The surface micro-hardness of carburized samples is improved significantly by about HK 400 compared with that of untreated materials. The total thickness of the hardened layer is about 300 μ m.

3) The carbon element, which appears either in the form of equiaxed TiC particles or as Ti–C solid solutions inside the α -Ti phase, leads to the decrease of hardness with increasing sample depth.

4) The limited influence of solid carburization on internal microstructure and hardness indicates that this method has the potential to strengthen the surface of titanium alloys and titanium matrix composites.

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固态渗碳对 Ti–6Al–4V 合金及其复合材料 (TiB+La₂O₃)/Ti–6Al–4V 表面显微组织和硬度的影响

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摘 要: 以 Ti–6Al–4V 合金和(TiB+La₂O₃)/Ti–6Al–4V 复合材料为研究对象, 研究固态渗碳法对两种材料表面显微组织和硬度的影响规律。将包覆于石墨粉中的试样置于密封的石英管中, 在 1227 K 下保温 24 h, 成功实现了两种材料表面渗碳处理。显微组织和物相分析结果表明, 固态渗碳后基体中原位生成了 TiC 增强体和 Ti–C 固溶体, 且扩散层中的等轴 α -Ti 相的体积分数随试样深度增加呈明显降低趋势; 硬度测试结果表明, 两种材料渗碳表面的显微硬度与未处理材料相比都明显提高了约 100%, 随试样深度增加而变化的碳含量在渗碳试样中形成了约 300 μm 的硬化层。同时, 固态渗碳对内部组织和硬度的影响很小, 表明该方法是一种有效强化钛合金及其复合材料的表面处理方法。

关键词: 钛合金; 钛基复合材料; 固态渗碳; 显微组织; 显微硬度

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