In situ TiC particles reinforced Ti6Al4V matrix composite with a network reinforcement architecture

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**Article history:**
Received 2 August 2010
Received in revised form 13 December 2010
Accepted 14 December 2010
Available online 22 December 2010

**Keywords:**
Titanium matrix composites (TMCs)
Network microstructure
Reaction hot pressing
Equiaxed microstructure
Mechanical properties

**Abstract**

TiC particles reinforced Ti6Al4V (TiCp/Ti6Al4V) composite with a network TiCp distribution has been successfully fabricated by reaction hot pressing of coarse Ti6Al4V particles and fine carbon powders. TiC particles are in situ synthesized around the boundaries of the Ti6Al4V particles, and subsequently formed into a TiCp network structure. Contrary to the typical Widmanstätten microstructure for the monolithic Ti6Al4V alloy, an equiaxed (\(\alpha + \beta\)) microstructure for the Ti6Al4V matrix of the composite is formed. This is due to the isotropic tensile stress generated by the network TiCp structure and the mismatch of coefficients of thermal expansion (CTE) during the phase transformation. The prepared composite exhibits superior compressive strength before and after heat-treatment due to the reinforcement network architecture and the relatively large matrix region with an equiaxed microstructure.

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1. Introduction

In the past two decades, discontinuously reinforced titanium matrix composites (DRTMCs) fabricated by \textit{in situ} methods have attracted much interest \cite{1-4} due to their superior and isotropic properties and low cost. Moreover, TiB whiskers (TiBws) and TiC particles (TiCps) synthesized by \textit{in situ} reactions have been proved to be the most effective reinforcements for Ti matrices \cite{2,5-7}. The mechanical properties of DRTMCs are not only determined by the volume fraction, morphology and type of reinforcement and matrix but also affected by the distribution of reinforcement and the morphology of matrix. It has been effectively demonstrated that the strengthening effect of reinforcement and the toughening effect of matrix can be better exploited by creating a network reinforcement architecture \cite{8,9}.

However, in the open literature, the influence of matrix morphology on the mechanical properties of DRTMCs has always been over-sighted despite that the quite different morphologies (equiaxed \(\alpha + \beta\) microstructure) of Ti6Al4V matrix in TiBw/Ti6Al4V composites have been reported recently \cite{8,10}. For the monolithic \(\alpha + \beta\) or near \(\alpha\) titanium alloys, it is common that a Widmanstätten lamellar microstructure is formed during cooling from above the \(\beta\) transus temperature. However, an equiaxed microstructure generally corresponds to a superior combination of mechanical properties over the Widmanstätten microstructure \cite{11}.

In the matrix of the DRTMCs fabricated by arc-melting \cite{12-14} or reaction hot pressing \cite{8}, an equiaxed \(\alpha + \beta\) microstructure can be always observed. Additionally, the titanium alloy matrix composites fabricated by gas-solid reaction \cite{15}, laser melting \cite{16} and powder metallurgy \cite{17,18} also present equiaxed microstructure in their matrix. The equiaxed microstructure cannot be eliminated by heat-treatment \cite{10,19}. In the TiCp reinforced composites, the previous interpretation for this phenomenon is that TiC particles hinder the growth of \(\alpha\) crystals parallel to specific crystallographic planes. In the TiBw reinforced composites, Gorsse and Miracle \cite{19} pointed out that the addition of TiB\textsubscript{2} to the Ti6Al4V matrix had an important effect on the formation of equiaxed \(\alpha\) phase. Other researchers \cite{8,10,20,21} believed that the whisker precipitate acted as the nucleation site of \(\alpha\) phase during the furnace-cooling following the sintering process and TiB whisker may also hinder the growth of \(\alpha + \beta\) lathes, which effectively restrict the formation of the Widmanstätten microstructure in the matrix. However, a recent study found that an equiaxed microstructure was also formed in the large TiBw-free matrix region without any reinforcement (particles or whiskers) \cite{8}. Therefore, the above growth hindering and nucleating roles played by the reinforcements cannot explain the phenomena \cite{8,10,15,18}.

The aim of the present work is to fabricate the \textit{in situ} TiCp/Ti6Al4V composite with a network reinforcement architec-
ture and to elucidate the formation mechanism of the equiaxed microstructure of titanium matrix observed in such composite in order to further comprehend the structure–property relationship of DRTMCs.

2. Experimental procedure

To fabricate TiCp/Ti6Al4V composite with a network microstructure requires the raw powder materials with a large difference in size to be low-energy milled instead of high-energy ball milling as used in the conventional powder metallurgy route. The spherical Ti6Al4V powder with a particle size of 180–225 μm (Fig. 1a) and fine carbon (C) powder (Fig. 1b) are selected. Firstly, the mixture of powders is milled at the speed of 200 rpm for 8 h using a planetary blender with low-energy under pure argon atmosphere. Fig. 1(c) shows SEM micrographs of the milled particles where the fine C powders are attached onto the surface of the large Ti6Al4V particle during the low-energy milling as illustrated by the insert sketch. Then the blended mixtures were hot pressed in vacuum (10^{-2} Pa) at 1200 °C under a pressure of 20 MPa for 60 min. During the hot pressing, TiC phase is in situ synthesized according to the following reaction [3]:

\[ \text{Ti} + \text{C} \rightarrow \text{TiC} \]  

(1)

For meaningful comparison, the monolithic Ti6Al4V alloy sample was also fabricated using the same raw Ti6Al4V powder and sintering parameters as those for TiCp/Ti6Al4V composites. It is clear that the typical Widmanstätten microstructure is formed and the size of the primary β grains is much larger (∼900 μm) than that of the as-received Ti6Al4V powder. For the α + β or near α two-phase Ti alloys, the formation of the Widmanstätten lamellar microstructure after cooling from above the β transus temperature is well documented [8,10,18]. The main reason for this phenomenon is that the new α phase has always grown along the direction with the lowest strain energy based on the theory of solid phase transformation. Therefore, the new α phase prefers to grow into the lamellar structure due to its special crystal structure, i.e., Widmanstätten microstructure. However, the formation of the Widmanstätten lamellar microstructure, particularly for the much large primary β grains, is believed to be harmful to the mechanical properties of titanium alloys [11]. In addition, the formation of much large primary β grains indicates that the original Ti6Al4V powders were merged during hot-press sintering process, and then the new primary β grains were formed from the merged β phase.

Compressive tests were carried out using an Instron-5569 universal testing machine at a constant crosshead speed of 0.5 mm/min. Compressive specimens have dimensions of ϕ6 mm × 9 mm and a total of five samples were tested for each material. Microstructural examination was performed by using a scanning electron microscopy (SEM, Hitachi S-4700).

3. Results and discussions

Fig. 1(d) shows the SEM micrograph of the monolithic Ti6Al4V alloy fabricated by using the same raw material and sintering parameters as those for TiCp/Ti6Al4V composites. It is clear that the typical Widmanstätten microstructure is formed and the size of the primary β grains is much larger (∼900 μm) than that of the as-received Ti6Al4V powder. For the α + β or near α two-phase Ti alloys, the formation of the Widmanstätten lamellar microstructure after cooling from above the β transus temperature is well documented [8,10,18]. The main reason for this phenomenon is that the new α phase has always grown along the direction with the lowest strain energy based on the theory of solid phase transformation. Therefore, the new α phase prefers to grow into the lamellar structure due to its special crystal structure, i.e., Widmanstätten microstructure. However, the formation of the Widmanstätten lamellar microstructure, particularly for the much large primary β grains, is believed to be harmful to the mechanical properties of titanium alloys [11]. In addition, the formation of much large primary β grains indicates that the original Ti6Al4V powders were merged during hot-press sintering process, and then the new primary β grains were formed from the merged β phase.

Ti + C → TiC

(1)
Fig. 1(e) shows the SEM micrographs of TiCp/Ti6Al4V composite with a network microstructure where the TiC particles are distributed around the deformed Ti6Al4V particles forming a “grain boundary”-like structure with the “grain” size of about 200 μm which is equal to the size of as-received Ti6Al4V particles [8,9]. For the matrix, due to the existence of the TiCp network, the coarsening of the primary β grain is limited in the Ti6Al4V matrix particle which is much smaller than the primary β grain formed in the monolithic alloy [Fig. 1e]. That is to say, the existence of the TiCp network can effectively restrict the formation of the coarse primary β grains for two-phase Ti alloys after sintering at 1200 °C (higher than the β transus temperature), which is beneficial to the mechanical properties [11]. Moreover, the equiaxed α phase is formed in the reinforcement-free matrix instead of the Widmanstätten lamellar microstructure observed for the monolithic Ti6Al4V alloy (Fig. 2a). This equiaxed microstructure can further improve the mechanical properties of the composite. Although, a similar microstructure feature, i.e., equiaxed α phases and intergranular β phase was observed in the TiCp/Ti6Al4V [15,17,18] and TiBw/Ti6Al4V composites [8,10,19,20], the formation mechanism of the equiaxed microstructure proposed in these previous work cannot help explain the present observation due to the absence of reinforcement in the matrix.

The formation mechanism of equiaxed microstructure of titanium matrix observed in the present work can be elucidated as following: the stiffer TiCp network can effectively constrain the shrinkage of the softer Ti6Al4V when cooling from 1200 °C and the phase transformation from β phase (bcc) to α phase (hcp). This formed an isotropic tensile stress state within the entire Ti6Al4V matrix particles of the composite. The existence of tensile stress is effectively demonstrated by the severe stress corrosion during the specimen etching as shown in Fig. 3. It has been shown that, during solid state transformation, the phase transformation and phase growth can be strongly affected by the existence of tensile stresses [23,24]. In the present system, the stiffer TiCp network shell or the isotropic tensile stress can effectively constrain the new α phase nucleation and growth during cooling process. On the one hand, this constraining effect is beneficial to the formation of the equiaxed microstructure. On the other hand, this constraining effect can decrease the phase transformation temperature, decreasing the phase transformation temperature can increase the nucleation rate, which can further cause the formation of the equiaxed microstructure. Therefore, the formation of the equiaxed α phase can be attributed to the isotropic tensile stress caused by the stiffer network. Additionally, it is believed that the different coefficients of thermal expansion (CTE) of Ti matrix and TiCp reinforcement can intensify the isotropic tensile stress, which contributes to the formation of the equiaxed α phase.

Based on the theory of solid phase transformation developed for metallic alloys [25], such as the monolithic Ti6Al4V alloy, the formation of lamellar phase (Widmanstätten microstructure) is due to a lower strain energy than that of equiaxed microstructure. This is mainly controlled by the elastic strain energy (ESE), which is generated by the different specific volume of new phase and parent phase in the metal alloys. However, in the composites, the ESE of matrix is affected by the tensile stress which generated a higher ESE than that generated by matrix phase transformation from β phase to α phase. Therefore, the higher ESE dominates the morphology of matrix in the composite, which causes the formation of equiaxed microstructure. That is to say, the formation of equiaxed microstructure in the matrix of composite is caused by the existence of the isotropic tensile stress state generated due to the presence of reinforcement network and the different CTEs of reinforcement and matrix, given the absence of reinforcement in the large matrix.

Fig. 4 shows the compression test results for TiCp/Ti6Al4V composite and the monolithic Ti6Al4V alloy before and after heat-treatment in order to further investigate the contribution of the reinforcement network distribution and the matrix equiaxed microstructure to the mechanical properties. As expected, with a modest 5 vol.% TiC particles synthesized, the σ0.2 of the as-sintered composite increased from 850 MPa to 1060 MPa. The improved strength of the composite can be attributed to the special reinforcement distribution structure and the equiaxed microstructure of the matrix [8,9]. It is worth pointing out that the composite is fabricated just by the simplified process, i.e., low-energy milling and one-step sintering, without any subsequent processing such as extrusion, forging or heat-treatment after the sintering process.

After heat treatment, σ0.2 of the monolithic Ti alloy and composite are increased from 850 MPa and 1060 MPa to 1105 MPa and 1356 MPa, respectively. That is to say, heat treatment increased the mechanical properties of TiCp/Ti6Al4V composite in comparison to the monolithic Ti6Al4V alloy.
the $\sigma_{0.2}$ of the monolithic Ti alloy and TiCp/Ti6Al4V composite by 30% and 33%, respectively. The increment in $\sigma_{0.2}$ of the composite (33%) is even slightly bigger than that of the monolithic Ti6Al4V alloy (30%), at a higher level (1060 MPa). Together with our previous report of TiBw/Ti6Al4V composite [8], the prominent heat-treatment strengthening effect should be attributed to the existence of the large reinforcement-free matrix region. Moreover, the slightly bigger increment (33%) of the $\sigma_{0.2}$ of the composite just can be attributed to the equiaxed microstructure of matrix in the composite with a network microstructure.

4. Conclusions

(1) TiCp/Ti6Al4V composite with a network microstructure has been successfully fabricated by choosing as raw materials, large Ti6Al4V and fine C powders and a simplified process involving low-energy milling and one-step sintering.

(2) Equiaxed ($\alpha$ + $\beta$) microstructure is formed instead of the typical Widmanstätten microstructure even in the central matrix without reinforcement of the TiCp/Ti6Al4V composite. This phenomenon can be attributed to the isotropic tensile stress generated by the network TiCp reinforcement structure and their different CTE.

(3) The prepared composite exhibits superior strength due to the reinforcement network distribution and the large reinforcement-free matrix region. Moreover, the equiaxed $\alpha$ + $\beta$ microstructure of the matrix region can further improve the strength of the composite with a network microstructure before and after heat-treatment.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (NSFC) under grant no. 50771039 and the Royal Society (RS)-NSFC International Joint Project under grant no. 5101130206. Huang is supported to study at the University of Bristol for one year through China Scholarship Council (CSC).

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