High Temperature Properties of Discontinuously Reinforced Titanium Matrix Composites: A Review

Lin Geng · Lujun Huang

Received: 27 May 2014/Revised: 21 August 2014/Published online: 9 October 2014
© The Chinese Society for Metals and Springer-Verlag Berlin Heidelberg 2014

Abstract Further improvement on high temperature durability is one of the most important aims except for high specific strength, high specific stiffness, and excellent wear resistance, to design and fabricate discontinuously reinforced titanium matrix composites (DRTMCs). Their superior properties render them extensive application potential in aerospace and military industries due to the urgent demand for the materials with characteristics of lightweight, high strength, high stiffness and high temperature durability. With development on fabrication methods and room temperature properties, testing, characterizing, evaluating and further increasing high temperature properties of DRTMCs are becoming more and more important to promote their applications. This review provides insights and comprehensions on the high temperature tensile properties, superplastic tensile properties, creep behaviors, and high temperature oxidation behaviors of DRTMCs, and research proposals to further improve the high temperature properties of DRTMCs are given.

KEY WORDS: Titanium matrix composites; High temperature tensile properties; Creep behaviors; Oxidation behaviors; Superplasticity

1 Introduction

Discontinuously reinforced titanium matrix composites (DRTMCs) possess high specific strength, specific stiffness, wear resistance and high temperature durability, which render them extensive application potential in aerospace, weapon, automotive, and so on [1–4]. In fact, the main aim of developing DRTMCs is to widen the utilization field at high temperatures by increasing their high temperature properties such as oxidation resistance,

strength, creep resistance, service temperature, etc., on the basis of titanium alloys [5–7]. In the past several decades, most of researches focused on the fabrication methods, reinforcement, interface, and room temperature properties of DRTMCs, and powder metallurgy and vacuum casting technique are viewed as the two suitable fabrication methods [8–10]. In situ synthesized TiB whiskers (TiBw) and TiC particles (TiCp) are unanimously considered as the most effective reinforcements for the Ti matrix [1, 11–13] due to not only their high modulus and hardness, good chemical compatibility with Ti but also similar density and thermal expansion coefficient (CTE) with those of titanium. Moreover, the microstructure and interface characteristics between TiBw or TiCp and Ti matrix were clearly presented [14–17]. Based on the above successes, room temperature properties of DRTMCs including strength and ductility are significantly improved by using titanium alloys as matrix, tailoring reinforcement distribution, and performing hot deformation and heat treatment on DRTMCs in recent years [18–22].

Available online at <http://link.springer.com/journal/40195>

L. Geng (✉) · L. Huang (✉)
School of Materials Science and Engineering, Harbin Institute of
Technology, Harbin 150001, China
e-mail: genglin@hit.edu.cn

L. Huang
e-mail: huanglujun@hit.edu.cn

Fig. 1 Tensile properties of (TiB + TiC + La₂O₃)/Ti composites at high temperatures: **a** fracture strains; **b** tensile strengths [31]

However, the most important problem impeding the practical application of DRTMCs has already transferred to how to further improve their high temperature properties. Therefore, after the above remarkable development of DRTMCs, the subsequent work certainly focuses on how to characterize, evaluate and improve their high temperature properties. It is meaningful to review the progress on the high temperature properties of DRTMCs. Increasing the volume fractions of ceramic reinforcements and using high temperature titanium alloy as matrix are the two common routes to do this [1, 13, 18, 23]. The former probably improves the high temperature strength but would deteriorate their ductility and oxidation resistance. The latter would effectively increase their high temperature strength and service temperature.

However, significant improvements on strength and oxidation resistance can be achieved by tailoring the network distribution of ceramic reinforcements according to our recent work [9, 24]. In particular, the ultimate tensile strength of TiBw/Ti60 composites with a network microstructure can be increased to almost 1,000 and 800 MPa at 600 and 700 °C, respectively. The smooth oxidation scale without any spallation and detachment of the network structured TiCp/Ti6Al4V composites after holding for 100 h at 700 °C constructs a strong contrast to the serious spallation scale of Ti6Al4V alloy after 40 h in our previous work [25], which visually confirmed the improved oxidation resistance by tailoring network distribution of TiCp reinforcement.

In this paper, the recent research progress on high temperature tensile behaviors, creep behaviors, and high temperature oxidation behaviors are reviewed. In addition, the existing problems in the present research are also revealed and then the further research directions in future are proposed.

2 High Temperature Tensile Behaviors

At high temperatures, strength is more important than ductility for DRTMCs. Increasing the volume fractions of

reinforcement [1, 26] and employing high temperature titanium alloy as matrix [13, 23, 27, 28] are the two main routes to improve the high temperature strength of DRTMCs. It is well known that the ceramic reinforcements possess much higher melting temperature, strength, modulus and hardness compared with titanium matrices. Therefore, adding ceramic reinforcements is expected to enhance the high temperature strength of DRTMCs. Fortunately, DRTMCs especially reinforced by TiBw or TiCp exhibited a much higher strength compared with the monolithic titanium alloy below some critical temperatures by load-bearing effect of reinforcement [9, 29, 30].

Kondoh et al. [30] investigated high temperature properties (200–400 °C) of TiC(CNTs)/Ti composites fabricated by spark plasma sintering and hot extrusion. The results showed that the matrix grains were remarkably refined by the pinning effect of TiC reinforcement, which positively contributes to the improvement of high temperature mechanical properties. The prepared composites exhibited higher strength due to the dispersion strengthening mechanism of the second phases and the grain refinement effect. The reason is that the in situ TiC reinforcement can effectively retard grain boundary sliding and matrix grain recrystallization and inhibit matrix grain coarsening at high temperatures. Therefore, the high temperature strength of the composites increases with increasing the reinforcement volume fractions.

Xiao et al. [31] investigated tensile properties at 600–700 °C of a multiple (TiB + TiC + La₂O₃)/Ti composites fabricated by casting and forging technology. As shown in Fig. 1, the results showed that the composites exhibited higher strength and fracture strain than (TiB + TiC)/Ti composites with the same volume fraction of reinforcement. Moreover, the 2.4 vol% (TiB + La₂O₃)/Ti composites with the lowest reinforcement volume fraction exhibited the highest strength at 650 and 700 °C, the highest fracture strains at all temperatures even higher than Ti matrix alloy, which can be attributed to the efficient strengthening effect of TiBw, microstructure refinement,

Fig. 2 Tensile stress–strain curves **a**, tensile properties **b** of TiBw/Ti composites in the range of room temperature to 900 °C [33]

Fig. 3 SEM images showing the longitudinal sections near the fracture surfaces of the TiBw/Ti composite sheet tested at 600 °C **a**; 900 °C **b** [33]

and adsorbing oxygen of La rare earth element. These two phenomena sufficiently demonstrate the positive role of La_2O_3 phase in strengthening and toughening effects. That is to say, the significant strengthening effect can be attributed to the load-bearing effect of TiBw and dispersion strengthening effect of TiC and La_2O_3 particles [31]. Therefore, not only reinforcement volume fraction but also reinforcement morphology and type determine the strength of the composites.

Wang et al. [32] also reported that load-bearing effect of TiC reinforcement with a long strip shape is more evident than that with an equiaxed morphology. In addition, they also pointed out that TiC reinforcement fracture exploiting load-bearing effect dominates the damage of the composites at 700 °C, while void nucleation, growth and coalescence indicating interface debonding are the main fracture mechanism above 800 °C. It is certain that the composites with the highest reinforcement volume fraction exhibit the highest tensile strength at high temperatures. They finally concluded that the strengthening mechanisms of the in situ TiC/Ti composites

include solid solution of C element in matrix, load-bearing of TiC reinforcement, dislocation strengthening effect.

However, strengthening effect remarkably decreases due to the interfacial debonding, which is attributed to the weakening effect of the interface and matrix. Therefore, using high temperature titanium alloy as matrix or enhancing the high temperature strength of titanium matrix is the key factor to further enhance the service temperature of DRTMCs. Using TA15 titanium alloy with a service temperature of 500 °C as matrix, the strength of TiCp/TA15 composites is increased to 625, 476 and 342 MPa, respectively at 600, 650 and 700 °C [23]. Moreover, the strength of TiBw/Ti composites is increased to 850, 740 and 490 MPa, respectively at 600, 650 and 700 °C by using Ti–6Al–2.5Sn–4Zr–0.7Mo–0.3Si–0.2Y alloy as matrix and rolling deformation as shown in Fig. 2 [33]. Although the composites exhibited higher strength compared with the matrix alloy below 700 °C, the strength of the composites become comparable with that of the matrix alloy due to the significant decrease of matrix strength at 750–900 °C.

Fig. 4 Comparison of high temperature tensile strength between TiBw/Ti6Al4V composites with network microstructure and the monolithic Ti6Al4V alloy [9]

By detailed microstructure analysis, they concluded that the decrease tendency of the strength with increasing temperatures could be attributed to recovery at 600 °C, dynamic recrystallization (DRX) at 700 °C, grain coarsening, and dislocation climb above 800 °C. As shown in Fig. 3, higher strengthening effect corresponds to the reinforcement fracture combining with dimples, however, lower strengthening effect is related to the interfacial debonding through generation, growth, and connection of voids.

Furthermore, the strength can be increased to 889 and 721 MPa at 600 and 700 °C by using Ti60 alloy with the highest service temperature of 600 °C [24]. It is worth pointing out that the reinforcement distribution plays an important role in improving the high temperature strength. In our previous work [9], the service temperature can be remarkably increased by 200 °C based on the similar tensile strength, as shown in Fig. 4. In addition to reinforcement, the main reason for the improved high temperature durability is attributed to that the weakening effect of grain boundary at high temperatures can be inhibited by introducing ceramic reinforcement into grain boundary (network microstructure). Furthermore, the highest strength of the as-sintered composites reported in literatures at 600 and 700 °C belongs to TiBw/Ti60 composites with a network microstructure, which can further confirm the contribution of the reinforcement distribution and the high temperature titanium alloy as matrix. In addition, the whisker and branched morphologies of reinforcements certainly play positive roles in improving the strengthening effect [9]. Additionally, rare earth elements are believed to improve the tensile properties by adsorbing the oxygen in matrix and refining the microstructure, which can play dispersion strengthening effect [31].

The subsequent deformation and heat treatment can effectively enhance the tensile strength of DRTMCs by

aligned reinforcement distribution, matrix work hardening effect and heat treatment strengthening effect below some critical temperature. Moreover, the conditions of heat treatment and deformation also affect the strengthening effect [22, 34–36]. The tensile strength of TiBw/Ti6Al4V composites with network microstructure can be significantly increased to almost 1,000 and 900 MPa at 400 and 500 °C, respectively, just by proper heat treatment [35]. Recent experiment results show that for the TiBw/Ti60 composites with network microstructure, the strength can be further enhanced to almost 1,000 and 800 MPa at 600 and 700 °C, respectively, after extrusion deformation. In general, the superior tensile strength of DRTMCs after hot deformation such as forging, rolling and extrusion and heat treatment is related with the strengthening effect of heat treatment and deformation. However, this improvement almost disappeared above some critical temperature, such as 600 °C for Ti6Al4V matrix composites [35], 750 °C for Ti–6Al–2.5Sn–4Zr–0.7Mo–0.3Si–0.2Y matrix composites [33], 800 °C for Ti60 matrix composites, which is attributed to the matrix softening effect and disappearance of work hardening effect. The matrix softening above the critical temperature is mainly attributed to phase transformation from α phase to β phase, and also related to the decrease of dislocation density and interatomic forces at high temperatures. In addition, recovery, DRX and dislocation climb are responsible for the strength degradation above the critical high temperature [32, 33].

In summary, the strengthening mechanisms of DRTMCs include the load-bearing strengthening, dispersion strengthening, dislocation strengthening, and solid solution strengthening. In addition, microstructure refinement is beneficial to strengthening the composites at relatively high temperatures. When the tensile temperature is lower than the critical temperature, all the above strengthening effects can play an important role in improving the strength of the composites.

In addition, although ductility is not a considerable question for DRTMCs, superplasticity of DRTMCs is still an important factor which can reveal their deformability and application field. In general, the superplasticity of DRTMCs is lower than that of the matrix alloy due to the introduction of hard reinforcement. However, the superior superplasticity of DRTMCs are frequently reported in recent years [37–41]. Lu et al. [42] reported a maximum elongation of 462% for the 5 vol% (TiBw + TiCp)/Ti6Al4V composites at 920 °C. Wang et al. [43] reported a maximum elongation of 429% for 1 vol% (TiBw + TiCp)/Ti1100 composites at 980 °C. Even, a maximum elongation of 659% was obtained at a very low temperature of 800 °C for the 5 vol% (TiC + TiB)/Ti composites fabricated by casting and forging technology [39]. It was also pointed out that the addition of reinforcements reduced the

superplastic temperature, which is beneficial to superplastic deformation of the composites. In addition, hydrogen can increase optimum superplastic strain rate and decrease optimum superplastic deformation temperature by increasing the amount of β phase and decreasing the β transus temperature of the composites, however, the superplastic mechanism of grain boundary sliding keeps unchanged [38]. The network structured TiBw/Ti6Al4V composites also exhibited a tensile superplasticity of 216%. It is worth pointing out that this superplasticity is obtained under absence of protective enamel [44].

Based on the above literatures, the superplastic mechanism of DRTMCs is mainly related to be phase/grain boundary sliding, grain boundary diffusion, grain rotation, dislocation movement and DRX. However, the effects of reinforcements on the superplasticity of the composites are still not clear and need further investigation.

3 Creep Behaviors

Numerous literatures showed that DRTMCs exhibited larger creep stress exponents and higher creep activation energies compared with the monolithic titanium alloys [1, 45, 46], which means the enhancement of creep resistance. This phenomenon can be mainly attributed to the existence of hard ceramic reinforcements, which obviously impede the creep deformation of DRTMCs. Therefore, an extra threshold stress (σ_0) arises for creep deformation of DRTMCs. That is to say, the creep deformation of DRTMCs is determined by not the applied stress (σ) but an effective stress ($\sigma_c = \sigma - \sigma_0$) [1]. It is unanimous that the threshold stress increases with increasing the volume fractions of ceramic reinforcements. However, Ma et al. [47, 48] also reported that the threshold stress disappeared for in situ 15 vol% TiBw/Ti composites and ex situ 15 vol% TiCp/Ti6Al4V composites at 873–923 K. It is believed that the threshold stress determines the creep stress exponent, which therefore increases with increasing the volume fractions of reinforcement. As reported by Tsang et al. [49], the creep stress exponent increases from 4.2 to 6.2 when the TiBw fraction increases from 0 to 15 vol%. Ranganath and Mishra [50] also reported high stress exponents ranging from 6 to 7 at 823 K for (TiB + Ti₂C)/Ti and Ti₂C/Ti composites owing to the transition of creep mechanism from lattice to pipe diffusion-controlled dislocation climb. Even, abnormally high stress exponents ranging from 8.1 to 14.3 at 823–873 K are reported for ex situ 15 vol% TiCp/Ti6Al4V composites in [48]. In addition, the creep rates of DRTMCs significantly decrease compared with the monolithic titanium alloy under the identical stresses and temperatures. Tsang et al. [49] reported that the creep rates of in situ TiBw/Ti

composites were between one and three orders of magnitude lower than the matrix material. Ma et al. [47] also reported that the creep rate of in situ TiBw/Ti composites was about one order of magnitude lower than that of the monolithic titanium material at 923 K. In summary, the creep properties can be improved by introducing ceramic reinforcements and increased with increasing the volume fractions of reinforcements.

Liu et al. [51] claimed that the creep resistance of the 10 vol% TiCp/TA15 composites prepared by laser melting deposition process is significantly increased compared with the monolithic matrix alloy at 600 and 650 °C, which is attributed to the load transfer from the matrix to the reinforcements and the refinement of matrix microstructure. The 10 vol% TiCp/TA15 composites exhibited significant improvement on the creep rupture lives compared with the 8 vol% (TiB + TiC)/Ti6242 composites reported in [52]. The analysis about creep rupture behaviors indicates that the creep rupture mechanism of the in situ TiCp/TA15 composites is associated with a mixture of particle cracking, interface debonding and interparticle voiding. Moreover, voids nucleated at broken particles, debonded interfaces and interparticle matrix at the initial stage of rupture. The final creep failure of the composites is still related to the ductile failure through the growth, coalescence and transverse linkage of the voids in the matrix.

In order to further improve the creep properties of DRTMCs, Xiao et al. [53, 54] selected near alpha high temperature titanium alloy (IMI 834) with the highest service temperature of 600 °C as matrix and the hybrid (TiBw + TiCp) and La₂O₃ as reinforcements to fabricated (TiBw + TiCp + La₂O₃)/Ti composites and (TiBw + La₂O₃)/Ti composites by casting and hot working technologies. It was reported that the composites exhibited a significant enhancement in creep resistance, accompanied by higher stress exponents compared with the matrix alloy. As shown in Fig. 5, the threshold stresses of DRTMCs always exist in both low stress region and high stress region, while they are much higher in high stress region compared with those in low stress region. It is worth pointing out that the threshold stress increases with decreasing the temperatures.

After considering the threshold stresses, the compensated activation energies of the composites can be reduced, which are lower than those of the matrix alloy both in the low stress region and in the high stress region, as shown in Fig. 6.

Except for the reinforcements and matrix types, the heat treatment and hot deformation can also improve the creep properties by changing the matrix microstructure. As reported by Li et al. [34], the creep resistance of the (TiBw + La₂O₃)/Ti composites after the TRIPLEX heat treatment is slightly lower than that after β heat treatment due to microstructure refinement.

Fig. 5 Creep data compensation of DRTMCs with threshold stresses: **a** low stress region; **b** high stress region [53]

Fig. 6 Arrhenius plots of the logarithmic creep rates versus the reciprocal Kelvin temperature for the matrix alloy and DRTMCs at effective constant stresses [53]

The microstructure evolution of the composites after creep deformation clearly confirmed that the hybrid reinforcements effectively impeded the dislocation movement in the high stress region, while the impeding effect is significantly degraded in the low stress region [53, 54]. The calculated results of stress transfer coefficient indicate that the stress transfer effects of reinforcements increase with increasing the temperatures. Therefore, the threshold stresses at lower temperatures and stress transfer effects at higher temperatures are responsible for the improvement of creep resistance in the DRTMCs [53, 54].

4 High Temperature Oxidation Behaviors

It can be confirmed that the oxidation behaviors are influenced by extrinsic factors such as oxidation temperature and oxidation form (continuous in thermal gravity analyzer (TGA) [55, 56] or discontinuous in air furnace [5, 57, 58]) and intrinsic factors such as matrix composition and reinforcement type, volume fraction and distribution.

Zhang et al. [55] investigated the oxidation behaviors of a Ti-6Al-1.2B alloy (i.e., 6.3 vol% TiBw/Ti6Al

composites) fabricated by casting technology in the range of 600–950 °C using a Seiko 320 DTA-TG. The accurate data showed that the oxidation behavior of the 6.3 vol% TiBw/Ti6Al composites obeyed the parabolic law; moreover, the oxidation process with activation energy of 250 kJ/mol was mainly controlled by both the outward diffusion of Ti and inward diffusion of O through the oxidation scale. As shown in Fig. 7, pores at the interface of TiBw–Ti and within the matrix, even cracks were formed by the interconnecting pores. This phenomenon indicated that the TiBw reinforcement probably reduces the oxidation resistance of the composites by evaporation of B_2O_3 during oxidation:

In addition, Zhang et al. [55] also pointed out that the oxygen diffusion along the interface of TiBw–Ti was easier and faster than that within the matrix alloy, which reduced the oxidation resistance of the composites. However, they did not compare the oxidation resistance of the composites with that of the corresponding Ti–6Al alloy.

In a recent work, Hu et al. [59] further confirmed that the oxidation resistance of the TiBw/Ti60 composites was indeed deteriorated through comparing the weight–gain curves of the composites and the matrix alloy due to the easier and faster diffusion of O element. Moreover, they pointed out that not only the interface but also the unstable region including phase boundary and residual stress field formed around TiBw during the fabrication process was easily oxidized when compared with the matrix alloy far away from TiBw. Furthermore, the oxidation resistance decreased with increasing volume fractions of TiBw due to the increasing interface and grain boundary.

Zhang et al. [56] investigated the oxidation behavior of in situ 10 vol% TiCp/Ti6Al composites in the range of 600–800 °C using a TGA. They found that the in situ composites exhibited a superior oxidation resistance at 600 and 700 °C, but their oxidation resistance is tremendously decreased at 800 °C. Certainly, the oxidation behavior of

Fig. 7 Cross-sectional microstructure of 6.3 vol% TiBw/Ti6Al composites formed after oxidation for 50 h at 750 °C **a**; 800 °C **b** [55]

Fig. 8 SEM images of TiC in TiC/Ti composites **a**; TiC **b**; Nd₂O₃ **c** in (TiC + TiB + Nd₂O₃)/Ti composites after oxidation [58]

the composites always obeys the parabolic law due to the continuous oxidation condition in TGA. In addition, TiC reinforcement can be oxidized according to the following equation:

The oxidation of TiC reinforcement was further certified by investigating the oxidation behaviors of TiC/Ti, (TiB + TiC)/Ti-7.26Al and (TiB + TiC)/Ti6242 composites with different volume fractions of reinforcement in the range of 550–650 °C [5, 57, 60]. However, introduction of TiC reinforcement can effectively decrease the oxidation rate and improve the oxidation resistance of the TiC/Ti composites compared with pure Ti due to the formation of the continuous and integrated oxide scales without spallation. Moreover, the size of TiO₂ decreased with increasing the volume fractions of TiC reinforcement by providing high surface areas to oxygen and reducing the internuclear distance, which further decreased the oxidation rate of the composites [5, 13, 60]. The reason is that the cracking and spallation of oxidation scales can be avoided by releasing the growth and thermal stresses through deformation and creep of the scales with small size of TiO₂ [5, 57, 60, 61]. Qin et al. [5, 60] also revealed that the

scales consisted of three sublayers due to the addition of Al element: the outermost layer of TiO₂, then Al-rich layer of Al₂O₃ and TiO₂ mixture, and inner Ti-rich layer of Al₂O₃ and TiO₂ mixture. A continuous Al₂O₃ or Al₂O₃-rich outermost layer easily formed in DRTMCs with the matrix containing Al due to the fast outward diffusion of Al element, which can effectively enhance the oxidation resistance of the DRTMCs due to the superior oxidation resistance of Al₂O₃ layer [60]. In addition, the mechanical properties of substrate DRTMCs would be degraded due to the solid solution of oxygen as reported by Qin et al. [5, 60]. It can be concluded that the oxidation resistance of DRTMCs reinforced by TiCp is better than that reinforced by TiBw due to the evaporating B₂O₃.

Yang et al. [58] compared oxidation behaviors of multiple (TiC + TiB + Nd₂O₃)/Ti composites at 600 °C. The results showed that this kind of composites exhibited much lower oxidation rates and higher activation energy compared with TiC/Ti and TiC/Ti-6Al composites with different volume fractions of reinforcement, which means much higher oxidation resistance. Moreover, as the volume fractions of reinforcement increased, the oxidation rate and oxidation layer thickness decreased while the activation energy increased. As shown in Fig. 8, TiO₂ particles can be observed in the matrix and TiC surface, while no TiO₂

Fig. 9 SEM micrographs of oxidation surfaces at 700 °C for 100 h **a**, schematic illustration showing anti-oxidation mechanism of TiCp/Ti6Al4V composites with a network microstructure **b** [25]

particles on the smooth surface of the Nd_2O_3 reinforcement were detected. Furthermore, the TiO_2 layer on the surface of TiC reinforcement is finer and denser than that on the matrix surface. Therefore, Nd_2O_3 is the best; TiC is the better among the multiple reinforcements to improve the oxidation resistance of the composites. That is to say, the multiple reinforcements could effectively improve the oxidation resistance of the composites. In addition, Yang et al. [58] also pointed out that the internal stress in the matrix which was formed due to the different CTEs between the reinforcements and matrix could also stunt the diffusion of oxygen into the composites, resulting in improvement on oxidation resistance. However, this viewpoint is doubtable because the formed internal stress is tensile stress not compressive stress, which is considered to be harmful to oxidation or corrosion resistance by rapid short-circuit diffusion paths.

Liu et al. [62] investigated the oxidation behaviors of $\text{Mo}_2\text{C}/\text{Ti}$ and VC/Ti composites with different volume fractions in the range of 600–700 °C. The results showed that the addition of Mo_2C was beneficial to the oxidation resistance which was not changed with increasing the Mo_2C volume fractions. However, the addition of VC is detrimental to the oxidation resistance due to that the oxidation product of V_2O_5 is very volatile in the testing temperatures, which damages the protective role of the oxidation scale. In addition, they also reported that a small amount of Ti_3O oxidation product was formed besides TiO_2 according to XRD results.

In our previous work [25], TiCp/Ti6Al4V composites with a tailored network microstructure exhibited a superior oxidation resistance in the temperature range of 600–800 °C. The reasons for the improved oxidation resistance can be attributed to the following three factors as shown in Fig. 9. First, the network structures of the composites can divide the oxidation scale into very small units, which can significantly decrease growth and thermal stresses avoiding spallation of the oxidation scales. Second,

the prior formation of oxidation products near the interface of TiC-Ti can effectively peg the oxidation scales to avoid the detachment of the scales. Thirdly, self-assembled TiCp wall-structure can effectively block oxygen diffusion into inner matrix.

Velasco and Aswath [61] studied the oxidation behavior of 5.2 vol% TiBw/Ti8.5Al1Si composites in both flowing air and static air and found that the oxidation activation energy of the composites in static air was much higher than that in flowing air. That is to say, the oxidation resistance of the composites is decreased in flowing air, which is also an extrinsic factor.

According to the above results, researchers always claimed that the oxidation kinetic law of DRTMCs obeys the parabolic law [5, 55–58]. However, parabolic-linear and linear laws are also revealed and reported besides the parabolic law in recent years [59, 62, 63], as shown in Fig. 10. According to the characteristics of the parabolic law, the oxidation rate gradually decreases with increasing the oxidation time. Originally, the whole fresh surface of the specimen is presented in the high temperature oxidation environment, which results in the fastest oxidation rate. With the formation of the first oxidation scale, the oxidation rate remarkably decreases. Subsequently, the oxidation rate gradually decreases with increasing the thickness of the oxidation scale. These are attributed to the impeding effect of the growing oxidation scale to oxygen diffusion. Therefore, the perfect parabolic law corresponds to the integrated oxidation scale without any detachment and spallation at relatively low temperatures or continuous oxidation. The intrinsic reason is the relatively low stress due to the slow growth or absence of thermal stress which is just generated during cooling process. However, the integrated oxidation scale can be firstly formed and then detached at relatively high temperatures, which corresponds to the parabolic-linear law.

Furthermore, with further increasing the oxidation temperatures, it is probable that the integrated oxidation scale cannot be formed due to the very large growth and

Fig. 10 Mass gain–time relationship of monolithic Ti60 alloy, 1.7 vol% TiBw/Ti60 and 5.1 vol% TiBw/Ti60 composites at different temperatures: **a** 600 °C; **b** 700 °C; **c** 800 °C; **d** 900 °C [59]

thermal stress and other probable factors such as evaporation of oxidation products (CO_2 and B_2O_3). In fact, considering the evaporation of oxidation products such as CO_2 and B_2O_3 , the accurate oxidation law, oxidation products and oxidation activation energy cannot be obtained using the relationship between the mass gain and oxidation time in an open environment.

It should be pointed out that the ceramic reinforcements are not necessary to enhance the oxidation resistance of DRTMCs compared with the monolithic titanium alloy. If so, the oxidation activation energy of DRTMCs is probably lower than that of the monolithic titanium alloy [59]. First, some ceramic reinforcements are oxidized prior to the titanium matrix [56]. Second, some ceramic reinforcements such as TiBw would easily form the evaporating oxidation products which result in the formation of hole, crack and detachment of oxidation scale [55]. Finally, with increasing the volume fractions and decreasing the particle sizes of reinforcements, the interface of reinforcement and matrix and matrix grain boundary increase, which certainly decrease the oxidation resistance of DRTMCs due to the inferior oxidation resistance of the interface and grain boundary [55, 59]. In contrast, the prior formation of the

oxidation products on the boundary, interface or reinforcement can probably play an effective role in pegging the oxidation scales, which can indirectly improve the oxidation resistance by inhibiting the oxidation scale detachment and spallation [25]. Qin et al. [57] also confirmed the beneficial effect of the prior oxidation of crystal boundary by refining TiO_2 size. However, as the grain size decreased remarkably, prior oxidation along grain boundaries and phase interfaces could lead to rugged and rough interface in the composites [5, 60]. Therefore, before a continuous oxidation scale is formed, the oxidation kinetic depends on the grain size of matrix and the type, size, and volume fraction of reinforcements. After the formation of a continuous oxidation scale, the oxidation kinetic depends on the stunting effect of oxide scale on O element inward diffusion and Ti outward diffusion.

High temperature oxidation resistance of DRTMCs determines their application field and lifetime. Although some conclusions were deduced in the past investigations, such as oxidation kinetic law, oxidation products, oxidation scales, etc., research work on oxidation behaviors of DRTMCs is still insufficient. Moreover, most of the experimental results have not reached a consensus.

5 Summary and Future Outlook

- (1) Selecting near α high temperature titanium alloys as matrix, increasing volume fraction of reinforcement, tailoring architecture of reinforcement and subsequent hot deformation and heat treatment can effectively enhance the tensile strength of DRMTCS at high temperatures. However, the strengthening effects of reinforcement, deformation, and heat treatment become pale due to interface debonding at much high temperatures.
- (2) The ceramic reinforcements can effectively enhance the creep resistance of DRTMCs by impeding the creep deformation, which is attributed to the threshold stresses at lower temperatures and stress transfer effects at higher temperatures. Moreover, the threshold stresses of DRTMCs in high stress region are much higher than that in low stress region. In addition, the threshold stress increases with decreasing creep temperatures.
- (3) The oxidation resistance of DRTMCs decreases with increasing volume fractions of ceramic reinforcements such as TiB and VC which can form volatile oxides, while the oxidation resistance increases with increasing volume fractions of reinforcements such as TiC which can form fine and dense oxides. Therefore, the oxidation resistance of DRTMCs is mainly related to the quality, constituent of oxidation scale, and the volume fraction and distribution of reinforcements.
- (4) Designing and fabricating multi-scale architecture of multiple reinforcements and selecting high temperature titanium alloys as matrix are probably two effective routes to improve high temperature strength and creep resistance. Refining microstructure of matrix and reinforcement and improving distribution of reinforcement are beneficial to further increase the superplasticity of DRTMCs.

Acknowledgments This work was financially supported by the National Natural Science Foundation of China (Nos. 51101042, 51271064 and 51471063), the High Technology Research and Development Program of China (No. 2013AA031202) and the Fundamental Research Funds for the Central Universities (No. HIT.BRETH.201401).

References

- [1] S.C. Tjong, Y.W. Mai, Compos. Sci. Technol. **68**, 583 (2008)
- [2] X.L. Guo, L.Q. Wang, M.M. Wang, J.N. Qin, D. Zhang, W.J. Lu, Acta Mater. **60**, 2656 (2012)
- [3] L.J. Huang, L. Geng, H.X. Peng, K. Balasubramaniam, G.S. Wang, Mater. Des. **32**, 3347 (2011)
- [4] L.J. Huang, S. Wang, Y.S. Dong, Y.Z. Zhang, F. Pan, L. Geng, H.X. Peng, Mater. Sci. Eng. A **545**, 187 (2012)
- [5] Y.X. Qin, D. Zhang, W.J. Lu, W. Pan, J. Alloys Compd. **455**, 369 (2008)
- [6] Y.H. Liu, J.D. Hu, Y.P. Zhang, Z.X. Guo, Y. Yang, Acta Metall. Sin. (Engl. Lett.) **25**, 89 (2012)
- [7] W.J. Yao, X.L. Niu, L. Zhou, N. Wang, J. Lee, Acta Metall. Sin. (Engl. Lett.) **26**, 523 (2013)
- [8] I. Sen, S. Tamirisakandala, D.B. Miracle, U. Ramamurty, Acta Mater. **55**, 4983 (2007)
- [9] L.J. Huang, L. Geng, H.X. Peng, B. Kaveendran, Mater. Sci. Eng. A **534**, 688 (2012)
- [10] J.H. Wang, X.L. Guo, L. Xiao, L.Q. Wang, W.J. Lu, B.H. Li, Z.Q. Li, D. Zhang, Acta Metall. Sin. (Engl. Lett.) **27**, 205 (2014)
- [11] K. Morsi, V. Patel, J. Mater. Sci. **42**, 2037 (2007)
- [12] Z.Y. Ma, S.C. Tjong, L. Gen, Scr. Mater. **42**, 367 (2000)
- [13] W.J. Lu, D. Zhang, X.N. Zhang, R.J. Wu, T. Sakata, H. Mori, Mater. Sci. Eng. A **311**, 142 (2001)
- [14] W.J. Lu, D. Zhang, X.N. Zhang, R.J. Wu, T. Sakata, H. Mori, Scr. Mater. **44**, 1069 (2001)
- [15] Q.C. Meng, H.B. Feng, G.C. Chen, R.H. Yu, D.C. Jia, Y. Zhou, J. Cryst. Growth **311**, 1612 (2009)
- [16] D.R. Ni, L. Geng, J. Zhang, Z.Z. Zheng, Mater. Lett. **62**, 686 (2008)
- [17] W.J. Lv, L. Xiao, K. Geng, J.N. Qin, D. Zhang, Mater. Charact. **59**, 912 (2008)
- [18] C.J. Zhang, F.T. Kong, S.L. Xiao, E.T. Zhao, L.J. Xu, Y.Y. Chen, Mater. Sci. Eng. A **548**, 152 (2012)
- [19] Z.X. Du, S.L. Xiao, P.X. Wang, L.J. Xu, Y.Y. Chen, H.K.S. Rahoma, Mater. Sci. Eng. A **596**, 71 (2014)
- [20] L.J. Huang, L. Geng, H.X. Peng, J. Zhang, Scr. Mater. **64**, 844 (2011)
- [21] L.J. Huang, L. Geng, B. Wang, H.Y. Xu, B. Kaveendran, Composites A **43**, 486 (2012)
- [22] B. Wang, L.J. Huang, L. Geng, Mater. Sci. Eng. A **558**, 663 (2012)
- [23] D. Liu, S.Q. Zhang, A. Li, H.M. Wang, J. Alloys Compd. **496**, 189 (2010)
- [24] L.J. Huang, F.Y. Yang, H.T. Hu, X.D. Rong, L. Geng, L.Z. Wu, Mater. Des. **51**, 421 (2013)
- [25] L.J. Huang, L. Geng, Y. Fu, B. Kaveendran, H.X. Peng, Corros. Sci. **69**, 175 (2013)
- [26] Y.J. Kim, H. Chung, S.J. Kang, Mater. Sci. Eng. A **333**, 343 (2002)
- [27] F.C. Ma, W.J. Lv, J.N. Qin, D. Zhang, Mater. Lett. **60**, 400 (2006)
- [28] Y. Wang, B. Lu, R. Yang, X.D. Han, P. Ren, Acta Metall. Sin. (Engl. Lett.) **25**, 95 (2012)
- [29] L. Geng, D.R. Ni, J. Zhang, Z.Z. Zheng, J. Alloys Compd. **463**, 488 (2008)
- [30] K. Kondoh, T. Threrujirapapong, J. Umeda, B. Fugetsu, Compos. Sci. Technol. **72**, 1291 (2012)
- [31] L. Xiao, W.J. Lu, Z.F. Yang, J.N. Qin, D. Zhang, M.M. Wang, F. Zhu, B. Ji, Mater. Sci. Eng. A **491**, 192 (2008)
- [32] H.W. Wang, J.Q. Qi, C.M. Zou, D.D. Zhu, Z.J. Wei, Mater. Sci. Eng. A **545**, 209 (2012)
- [33] C.J. Zhang, F.T. Kong, L.J. Xu, E.T. Zhao, S.L. Xiao, Y.Y. Chen, N.J. Deng, W. Ge, G.J. Xu, Mater. Sci. Eng. A **556**, 962 (2012)
- [34] J.X. Li, L.Q. Wang, J.N. Qin, Y.F. Chen, W.J. Lu, D. Zhang, Mater. Charact. **66**, 93 (2012)
- [35] L.J. Huang, H.Y. Xu, B. Wang, Y.Z. Zhang, L. Geng, Mater. Des. **36**, 694 (2012)
- [36] F.Y. Yang, A.B. Li, L.J. Huang, Y. Cheng, L. Geng, Rare Met. **30**, 614 (2011)
- [37] V. Sinha, R. Srinivasan, S. Tamirisakandala, D.B. Miracle, Mater. Sci. Eng. A **539**, 7 (2012)

- [38] J.Q. Lu, J.N. Qin, W.J. Lv, Y.F. Chen, D. Zhang, H.L. Hou, *Int. J. Hydrog. Energy* **34**, 8308 (2009)
- [39] M.M. Wang, W.J. Lu, J.N. Qin, D. Zhang, B. Ji, F. Zhu, *Scr. Mater.* **54**, 1955 (2006)
- [40] S. Roy, S. Suwas, *Mater. Des.* **58**, 52 (2014)
- [41] S. Roy, S. Suwas, *Mater. Sci. Eng. A* **574**, 205 (2013)
- [42] J.Q. Lu, J.N. Qin, Y.F. Chen, Z.W. Zhang, W.J. Lu, D. Zhang, *J. Alloys Compd.* **490**, 118 (2010)
- [43] M.M. Wang, W.J. Lu, J.N. Qin, D. Zhang, B. Ji, F. Zhu, *Scr. Mater.* **53**, 265 (2005)
- [44] L.J. Huang, Y.Z. Zhang, B.X. Liu, X.Q. Song, L. Geng, L.Z. Wu, *Mater. Sci. Eng. A* **581**, 128 (2013)
- [45] M.J.R. Barboza, E.A.C. Perez, M.M. Medeiros, D.A.P. Reis, M.C.A. Nono, F. Piorino, Neto, C.R.M. Silva, *Mater. Sci. Eng. A* **428**, 319 (2006)
- [46] S.I. Rhee, S.W. Nam, M. Hagiwara, *J. Alloys Compd.* **359**, 186 (2003)
- [47] Z.Y. Ma, S.C. Tjong, S.X. Li, *Metall. Mater. Trans. A* **32**, 1019 (2001)
- [48] Z.Y. Ma, R.S. Mishra, S.C. Tjong, *Acta Mater.* **50**, 4293 (2002)
- [49] H.T. Tsang, C.G. Chao, C.Y. Ma, *Scr. Mater.* **37**, 1359 (1997)
- [50] S. Ranganath, R.S. Mishra, *Acta Mater.* **44**, 927 (1996)
- [51] D. Liu, S.Q. Zhang, A. Li, H.M. Wang, *Mater. Des.* **31**, 3127 (2010)
- [52] W.J. Lu, D. Zhang, X.N. Zhang, R.J. Wu, T. Sakata, H. Mori, *Scr. Mater.* **44**, 2449 (2001)
- [53] L. Xiao, W.J. Lu, J.N. Qin, Y.F. Chen, D. Zhang, M.M. Wang, F. Zhu, B. Ji, *Compos. Sci. Technol.* **69**, 1925 (2009)
- [54] L. Xiao, W.J. Lu, J.N. Qin, Y.F. Chen, D. Zhang, M.M. Wang, F. Zhu, B. Ji, *Mater. Sci. Eng. A* **499**, 500 (2009)
- [55] E.L. Zhang, G. Zeng, S.Y. Zeng, *Scr. Mater.* **46**, 811 (2002)
- [56] X.N. Zhang, C. Li, X.C. Li, L.J. He, *Mater. Lett.* **57**, 3234 (2003)
- [57] Y.X. Qin, W.J. Lu, D. Zhang, J.N. Qin, B. Ji, *Mater. Sci. Eng. A* **404**, 42 (2005)
- [58] Z.F. Yang, W.J. Lu, J.N. Qin, D. Zhang, *Mater. Sci. Eng. A* **472**, 187 (2008)
- [59] H.T. Hu, L.J. Huang, L. Geng, C. Liu, B.X. Liu, B. Wang, *Corros. Sci.* **85**, 7 (2014)
- [60] Y.X. Qin, D. Zhang, W.J. Lu, W. Pan, *Mater. Lett.* **60**, 2339 (2006)
- [61] B.G. Velasco, P.B. Aswath, *J. Mater. Sci.* **33**, 2203 (1998)
- [62] Y.B. Liu, Y. Liu, Z.W. Zhao, Y.H. Chen, H.P. Tang, *J. Alloys Compd.* **599**, 188 (2014)
- [63] W.B. Li, M.H. Chen, S.L. Zhu, C. Wang, F.H. Wang, *Corros. Sci.* **87**, 179 (2014)