Chapter 2
Design and Fabrication of Network-Structured Pure Ti Matrix Composites

2.1 Design of Network-Structured Composites

In order to overturn the situation of inferior mechanical properties of discontinuously reinforced metal matrix composites (DRMMCs) fabricated by conventional powder metallurgy (PM), one quasi-continuous network microstructure of DRTMCs was successfully designed. As shown in Fig. 2.1 [1, 2], according to Hashin–Shtrikman (H–S) theory, the network microstructure in which the harder phase encapsulates the inner softer phase corresponds to the H–S upper bound [3, 4]. In addition, network microstructure is equivalent to introducing ceramic reinforcement into the grain boundary. On the one hand, this microstructure can enhance the grain boundary strengthening effect at room temperature. On the other hand, it can overcome the grain boundary weakening effect at high temperatures. Considering the failure to achieve superior tensile properties of the continuous ceramic network microstructure and the success of the bi-continuous microstructures of the Al MMCs, the local volume fraction of ceramic phase in the network boundary region should be controlled. Therefore, one noncontinuous network microstructure viewed from micro-field but continuous network microstructure viewed from macro-field, i.e., quasi-continuous network microstructure was successfully designed. Fabricating DRTMCs with the novel network microstructure requires the raw powder materials with a large difference in size to be low-energy milled instead of the high-energy milling as used in the conventional PM route [2, 5]. Using large size Ti powders not only can achieve the network microstructure, but also can retain virgin matrix region which can undertake strain and obstruct crack propagation. This is totally different with the conventional homogenous microstructure.

It is undoubted that in situ TiB whiskers (TiBw) and TiC particles (TiCp) are the most effective reinforcements for the Ti matrix [1, 6–8], and can lead to greater improvement in stiffness, strength, and creep resistance. However, in situ TiBw were chosen as the reinforcement, because they can decrease the local
reinforcement volume fraction to achieve quasi-continuous distribution of the reinforcement by growing into the inner matrix, which can also effectively joint the adjacent Ti matrix particles as a dowel connector. Additionally, the in situ TiB whiskers are viewed as the best reinforcement for the Ti matrix due to their high modulus, hardness, good chemical compatibility with Ti, and similar density and thermal expansion coefficient with the Ti matrix [1, 5, 6]. Therefore, one quasi-continuous network microstructure in which TiBw are uniformly distributed in the network boundary is designed for DRTMCs for performance improvement.

In order to obtain the designed quasi-continuous network microstructure, large spherical Ti powders as the Ti matrix and fine TiB2 powders as the B source for the TiBw reinforcement were selected. As shown in Fig. 2.2 [1], the fabrication route

![Design route of a quasi-continuous network microstructure for DRTMCs](image)

**Fig. 2.1** Design route of a quasi-continuous network microstructure for DRTMCs (Reprinted with the permission of Elsevier [1, 2])

![Flow chart showing the processing route together with morphologies of the raw materials and schematic illustrations of the network distribution](image)

**Fig. 2.2** Flow chart showing the processing route together with morphologies of the raw materials and schematic illustrations of the network distribution. a Large Ti powder, b fine TiB2 powder and the blended mixture at a lower c and higher d magnification; and schematic illustrations of network distribution e before and f after reaction synthesis (Reprinted with the permission of Elsevier [1, 9])
for TiBw/Ti composites with a network microstructure includes the simplified low-energy milling and reaction hot pressing processes.

The aim of low-energy milling is not to smash large Ti powders into fine powders but to adhere fine TiB2 powders onto the surface of large Ti powders/particles. In the present process, large Ti powders instead of fine Ti powders (5–20 μm) and low-energy milling instead of high-energy milling can not only guarantee the reinforcement network distribution, but also protect the Ti matrix from absorbing oxygen (O) and hydrogen (H) which can significantly increase the brittleness of the Ti matrix.

The TiB whiskers were in situ synthesized according to the following reaction equation [10]:

\[ Ti + TiB_2 \rightarrow 2TiB \]  

Molar mass: 47.96, 69.52, 117.42

Actual mass: \( \frac{47.96\text{wt}\% TiB_2}{69.52} \cdot X \)  

\( \frac{47.96\text{wt}\% TiB_2}{69.52} \cdot X \)  

On the basis of the Eq. (2.1), the correlation between the wt\% TiB2 added and the vol\.% TiBw synthesized can be expressed as the Eqs. (2.2) and (2.3).

\[
\text{vol\%TiB} = \frac{V_{TiB}}{V_{TiB} + V_{\text{remained-Ti}}} \times 100\% 
\]

\[
= \frac{117.42\text{wt}\% TiB_2 \cdot X}{69.52\rho_{TiB}} + \left( 1 - \frac{47.96\text{wt}\% TiB_2}{69.52\rho_{TiB}} \right) \cdot \frac{117.42\text{wt}\% TiB_2 \cdot X}{\rho_{Ti}} \frac{117.42\text{wt}\% TiB_2}{69.52\rho_{TiB}} \cdot X \]  

\[
= \frac{117.42\text{wt}\% TiB_2 \cdot X}{69.52\rho_{TiB}} + \left( 1 - \frac{47.96\text{wt}\% TiB_2}{69.52\rho_{TiB}} \right) \cdot \frac{117.42\text{wt}\% TiB_2 \cdot X}{\rho_{Ti}} \]  

where X is the total mass of the mixed material. Taking the \( \rho_{TiB} \) and \( \rho_{Ti} \) values of 4.5 and 4.45 g/cm\(^3\) for TiB density and Ti64 density into Eq. (2.3), the equation between wt\%TiB2 and vol\.%TiBw can be simplified to Eq. (2.4) [9].

\[
\text{vol\%TiB} = 1.7 \times \text{wt\%TiB}_2 
\]

According to the Eqs. (2.1) and (2.4), 1.7, 3.4, 5.1, 6.8, 8.5, and 10.2 vol\.% TiBw/Ti64 composites were designed and fabricated by adding 1, 2, 3, 4, 5, 6 wt\% TiB2 raw materials.

In order to design the optimal and the maximum volume fractions of reinforcement for TiBw/Ti composites with a network microstructure, two schematic illustrations of Ti and TiB2 mixture were constructed as shown in Fig. 2.3 [1, 10]. Figure 2.3a shows that half surface of every Ti particle is covered by fine TiB2 powders. For this case, all TiB2 powders have the same opportunity to contact with Ti particle when the loose mixtures are sintered to compact mixtures of Ti and TiB2. Then, the reaction between Ti and TiB2 can be rapidly completed, which causes the synthesis of coarse TiBw reinforcement [11]. In order to simplify the calculation process, the TiB2 powders were also assumed to be spherical due to their large size.
The difference between Ti and TiB$_2$ powders. For this case, the weight ratio of TiB$_2$ powder to Ti particle can be expressed as follows:

\[
m \cdot M = \frac{4}{3} \pi r^3 \cdot \rho_1 \cdot \frac{1}{2} \times \frac{4 \pi (R + r)^2}{\pi r^2} = \frac{2(R + r)^2 \cdot r \cdot \rho_1}{R^3 \cdot \rho_2}
\]

where \(m\), \(r\), and \(\rho_1\) are the weight, radius, and density of TiB$_2$ powders, respectively, and \(M\), \(R\), and \(\rho_2\) are those of Ti64 particles.

And then the calculation equation for the volume fraction \((V_{TiB})\) of in situ synthesized TiBw can be deduced by taking Eq. (2.6) into Eq. (2.4), which can be expressed as follows:

\[
V_{TiB} = \frac{3.4(R + r)^2 \cdot r \cdot \rho_1}{R^3 \cdot \rho_2 + 2(R + r)^2 \cdot r \cdot \rho_1}
\]

Taking the 100 \(\mu\)m \((R\) and 4.52 g/cm$^3$ \((\rho_2) values of the Ti particles and the 1.5 \(\mu\)m \((r\) and 4.45 g/cm$^3$ \((\rho_1) values of the TiB$_2$ powders, for example, the ‘optimal’ \(V_{TiB}\) can be calculated to be approximately 5.1 vol.%. Correspondingly, the optimal volume fraction of TiBw for the 55 \(\mu\)m \((R\) of the Ti particles is 8.5 vol.%. It is easy to consider that the ‘optimal’ volume fraction and the maximum increase with decreasing matrix particle sizes.

Accordingly, when the whole surface of the Ti64 particle is covered by TiB$_2$ powders as shown in Fig. 2.3b, the wt%TiB$_2$ and vol.%TiBw are 6 wt% and 10.2 vol.%. For this case, the outside of TiB$_2$ powder cannot easily touch with Ti and transformed to TiB whisker. Therefore, the reaction between Ti and TiB$_2$ can not be rapidly completed to synthesize coarse TiBw reinforcement. One similar phenomenal that fine TiBw and cluster TiBw formed when Ti is insufficient [12].

According to the calculation results, when the designed volume fraction of TiBw reinforcement is lower than the equal of 5.1 vol.%, just coarse and strong TiB whiskers are in situ synthesized. The strengthening effect increases with increasing
volume fraction of TiBw reinforcement. Once the volume fraction exceeds 5.1 vol.%, fine TiBw and even cluster TiBw formed, and the quantities of them increase with increasing the designed volume fraction according to the calculation results. In order to further demonstrate the calculation results and investigate the microstructure evolution, 1.7, 3.4, 5.1, 6.8, 8.5, and 10.2 vol.%TiBw/Ti64 composites were fabricated and analyzed as follows.

2.2 Fabrication of Network-Structured Composites

Based on the above consideration of quasi-continuous microstructure, large size Ti powder raw material, low-energy milling process and optimal reinforcement volume fraction, TiBw-reinforced pure Ti matrix composites with network microstructure were designed and fabricated. For comparison, 8.5 vol.%TiBw/Ti composites with homogenous microstructure were also fabricated using conventional high-energy milling process but the same raw materials and sintering parameters. In order to fabricate 8.5 vol.%TiBw/Ti composite with a conventional uniform microstructure, the spherical Ti powder with a large size had to be milled into fine powders with an average size of 10 μm by high-energy milling at the speed of 400 rpm and with a ratio of milled media to material of 10:1 for 15 h using a planetary blender, with adding 0.5 wt% process control agent (PCA) of stearic acid (CH₃(CH₂)₁₆COOH). It is well known that the PCA is necessary in order to avoid cold welding during high-energy milling process. It is certain that PCA can be thoroughly ejected by the exhaust process in vacuum (10⁻² Pa) at 400 °C for 40 min before the reaction hot pressing process (Because the boiling point of the PCA is 376 °C). That is to say, a two-step sintering process including the exhaust process and the reaction hot pressing process is necessary to fabricate the composites with a homogenous microstructure. For the fabrication of 5, 8.5 and 12 vol.% TiBw/Ti composites with a network TiBw distribution, Ti and TiB₂ powders were low-energy milled at a lower speed of 200 rpm and with a ratio of milled media to material of 5:1 for 8 h, without any PCA added. That is to say, the exhaust process can be omitted due to no PCA addition. Therefore, just one-step sintering process (reaction hot pressing process) is needed to fabricate the composites with a network microstructure. The reaction hot pressing process during both two-step and one-step sintering processes is hot pressing in vacuum (10⁻² Pa) at 1200 °C under a pressure of 20 MPa for 60 min. Both the high-energy milling and low-energy milling processes were protected under pure argon atmosphere [2].

Figure 2.4 shows the X-ray diffraction pattern of the as-sintered 8.5 vol.% TiBw/Ti composite indicating that only Ti and TiB phases exist in the as-sintered composites and no TiB₂ are detected [2]. Similar results were also obtained for other composites. This result demonstrates that the in situ reaction between Ti and TiB₂ was completed and in situ TiB/Ti composites were successfully fabricated. This result can also indirectly verify that the PCA added during the high-energy milling process was thoroughly ejected as mentioned above.
Figure 2.5 shows the SEM micrographs of the 8.5 vol.% TiBw/Ti composites with two different distributions of TiBw reinforcement [2]. In the composite fabricated by the high-energy milling and two-step sintering (the exhaust process and the reaction hot pressing process), the in situ synthesized TiBw is homogeneously distributed as shown in the Fig. 2.5a. However, in the composite fabricated by low-energy milling and one-step sintering (the reaction hot pressing process), TiBw is mainly distributed on the surface of “original” Ti powders/particles, and formed a network structure looking like “grain boundary” as shown in the Fig. 2.5b. The formation of network distribution can be attributed to the two reasons as mentioned in our previous work [1, 5, 13]: low-energy milling does not smash the large Ti powders (Fig. 2.2) and solid-state sintering restricts the reaction only on the surface of Ti particles (Fig. 2.2). Additionally, the selection of large spherical Ti powders is one another crucial factor, which guarantees the three-dimensional (3D) network
architecture. Additionally, many TiB whiskers grow into the inside of Ti particles like dowel connectors linking the neighboring Ti particles due to its special B27 structure [6, 14], which can effectively improve the strength and fracture toughness of TMCs. Additionally, due to the fine Ti powders smashed by high-energy milling and the uniform distribution of TiBw reinforcement, the matrix grain size of the composite with a homogenous microstructure is constrained about 20 μm as shown in Fig. 2.5a. This can be interpreted as following: the large spherical Ti powders were milled to fine powders with an average size of 20 μm. On the one hand, the crystal structure of the fine powder surface is damaged due to deformation [15]. On the other hand, the chemical compositions (Fe, O) of the fine powder surface are increased due to milling media of steel ball as shown in the Table 2.1 [2]. Therefore, the grain size of the composite is about 20 μm.

However, because the large spherical Ti powders are not broken out in the low-energy milling process, the matrix grain size of the composite with a network microstructure is constrained about 100 μm, which is equal to the size of the Ti raw material as shown in Fig. 2.5b. When the same strain, the dislocation density in the smaller matrix grain is higher than that in the larger matrix grain. Therefore, the composite with a network microstructure can bear much higher strain due to the large matrix grain, which is beneficial to the ductility of the composites.

Figure 2.6 shows the SEM micrographs of TiBw/Ti composites with different volume fractions but the same network distribution of TiBw reinforcement [1, 2]. It can be seen from Fig. 2.6 that the local volume fraction of TiBw in the network boundary increases with increasing the overall volume fraction. This means that the contiguity of reinforcement in network boundary increases, while the contiguity of matrix decreases with increasing the volume fraction. According to Wilkinson’s research [16], the strengthening effect of reinforcement increases but the toughening effect of matrix deceases with increasing the contiguity of reinforcement. Moreover, the agglomerations of reinforcement were formed due to excessive reinforcement in the network boundary of the 12 vol.%TiBw/Ti composite. It is certain that the network boundary is not absolutely continuous but interpenetrated between the adjacent matrix particles, which is beneficial to the ductility of the novel composites.

As shown in the magnified SEM micrograph (Fig. 2.7), in the network boundary, not only plain single TiBw but also branched TiBw can also be observed. So far, the branched structure of TiBw is only observed in the TMCs with the novel network distribution of TiBw [1, 2, 5]. It is certain that the branched reinforcement

<table>
<thead>
<tr>
<th>Powder</th>
<th>B</th>
<th>Cl</th>
<th>Na</th>
<th>Fe</th>
<th>Si</th>
<th>O</th>
<th>C</th>
<th>N</th>
<th>H</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>–</td>
<td>0.01</td>
<td>0.01</td>
<td>0.037</td>
<td>0.024</td>
<td>0.091</td>
<td>0.015</td>
<td>0.019</td>
<td>0.002</td>
<td>Balance</td>
</tr>
<tr>
<td>TiBw/Ti</td>
<td>1.61</td>
<td>0.01</td>
<td>0.01</td>
<td>0.21</td>
<td>0.023</td>
<td>0.13</td>
<td>0.018</td>
<td>0.021</td>
<td>0.003</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Table 2.1 Chemical compositions of Ti powders and 8.5 vol.%TiBw/Ti composites (wt%) (Reprinted with the permission of Elsevier [2])
structure is desirable, which is believed to be beneficial to improve the strengthening effect of reinforcement [17, 18]. Figure 2.8 exhibits the stress–strain curves of all the prepared TiBw/Ti composites and the monolithic pure Ti. First, the strength of the composites is always higher than that of the pure Ti, while the ductility of the composites is always lower than that of the pure Ti. The ultimate tensile strength ($\sigma_t$) of 12, 8.5, and 5 vol.% TiBw/Ti composites with a novel network microstructure and 8.5 vol.% TiBw/Ti composite with a conventional homogeneous microstructure is 907, 842.3, 753.8,
and 687.9 MPa, respectively, which are significantly improved than that (482.4 MPa) of the pure Ti. That is to say, \( \sigma_b \) of the four composites without any subsequent processing deformation such as extrusion has been increased by 88, 74.6, 56.3, and 42.6\%, respectively. However, the tensile elongation (\( \delta \)) of the composites reduced to 4.0, 11.8, 15.6, and 2.9\%, respectively, from 17.8\% of the pure Ti [2].

Second, it is surprised that not only the strength but also the ductility of the composites can be significantly improved by tailoring the network distribution of reinforcement. Both the strength and ductility (842.3 MPa and 11.8\%) of the 8.5 vol.\%TiBw/Ti composite with a network microstructure are much higher than those (687.9 MPa and 2.9\%) of the 8.5 vol.\%TiBw/Ti composite with a homogeneous microstructure. On the one hand, the design of the network architecture would increase the contiguity of reinforcement, which increases the strengthening effect of reinforcement. On the other hand, the large matrix particles retained during the low-energy milling process can improve the toughening effect of matrix by bearing strain and constraining the crack propagation. Additionally, the branched and dowel-like structures of TiBw reinforcement are beneficial to the strengthening effect, while the interpenetrating structure of matrix is beneficial to the toughening effect. Therefore, the novel network reinforcement architecture can exploit a superior combination of strengthening effect and toughening effect, simultaneously, than the conventional homogenous microstructure [2].

Third, the strength and elastic modulus of TiBw/Ti composites with a network microstructure increase with increasing the volume fraction of TiBw reinforcement from 5 to 12 vol.\%. In particular, the ultimate strength (\( \sigma_b \)) of 12 vol.\%TiBw/Ti composite is increased by 88\%, from 482 to 907 MPa. The remarkable improvement of strength appears to reveal the most effective strengthening effect for the DRTMCs up to date. Additionally, the strain hardening rate of the composites with a network microstructure decreases with increasing the volume fraction of reinforcement, which is also caused by increasing the contiguity of reinforcement.

![Fig. 2.8 The tensile stress–strain curves of the as-sintered TiBw/Ti composites with a network microstructure and a homogeneous microstructure and the pure Ti (Reprinted with the permission of Elsevier [2])](image)
Fourth, for the 5 and 8.5 vol.% TiBw/Ti composites with a network microstructure, the superior elongations of 15.6 and 11.8% appear to be the most effective improvements up to date, given the remarkable $\sigma_b$ increments of 56.3 and 74.6%, respectively. For the 12 vol.% TiBw/Ti composite, given the superior $\sigma_b$ increment of 88, 4.0% of elongation can be viewed as a superior improvement compared with that of the conventional DRTMCs with a homogeneous microstructure [1, 6, 7].

It is especially worth noting that the TiBw/Ti composites with a network microstructure is fabricated by a simplified process including low-energy milling and one-step sintering without any subsequent treatment such as extrusion or rolling. Therefore, the superior combination of strength and ductility for DRTMCs with a novel network microstructure can be attributed to the design of network microstructure, the branched and dowel-like structures of TiB whiskers, the retained large Ti matrix regions and the interpenetrating matrix structure crossing the network boundary.

Comparing with the conventional PM process including high-energy milling, isostatic cold pressing, two-step sintering process, and hot deformation in order to fabricate DRTMCs with a homogenous microstructure, the present simplified PM process just including low-energy milling and one-step sintering shows the following three advantages: First, the employment of large Ti powders instead of fine powders (5–20 µm) cannot only guarantee the network distribution microstructure but also decrease the raw material cost. Second, the low-energy milling instead of the high-energy milling did not smash large Ti powders into fine powders but adhere fine TiB₂ powders onto the surface of large Ti particles/powders, which can better exploit the toughening effect of matrix and decrease the processing period and cost. Thirdly, the isostatic cold pressing and exhausting processes, two necessary steps employed in the conventional PM process, can be removed by omitting PCA during low-energy milling, which can further reduce the sintering period and cost.

Additionally, Ti possesses a strong affinity for oxygen (O) and hydrogen (H), then easily becomes brittle by absorbing little O and H [19], which is another reason that DRTMCs fabricated by conventional PM process exhibit an extreme brittleness. In the present work, the large spherical Ti powders and low-energy milling can significantly reduce the absorption of O and H, compared with the irregular fine Ti powders and the high-energy milling process. Therefore, using the spherical Ti powders with a large size and the low-energy milling process to fabricate the TiBw/Ti composites with a network microstructure can overcome the severe drawback of DRTMCs. Therefore, the advantages of this novel route can be concluded as follows: improving mechanical properties, reducing the processing cost, shortening production period, simplifying fabrication process, manipulating microstructure, and achieving near net-shape products.

Figure 2.9 shows the SEM fractographs of 5 and 12 vol.% TiBw/Ti composites with a network microstructure. It can be clearly seen from Fig. 2.9a, c that the two overall fracture surfaces are very rough indicating torturous crack propagation path, which indicates an improved damage tolerance [20]. Herein, the flexible matrix
particle is not ruptured and the crack is always propagated along the network boundary. This observation adequately demonstrates that the network boundary dominates the behavior of the TiBw/Ti composite with a network microstructure [21], which is like the grain boundary strengthening effect. This is consistent with the superior strengthening effect of the reinforcement network microstructure. However, with increasing the volume fraction of reinforcement, fractured agglomeration of reinforcement increases but tearing ridge line decreases, which is due to the increasing local volume fraction of reinforcement in the network boundary as shown in Fig. 2.6. This observation corresponds to the decreasing ductility of the composites. In addition, it is worth pointing out that the abundant ceramic fracture of agglomeration as shown in Fig. 2.9c indicates that the low strain hardening rate is related to the agglomeration of reinforcement caused by the high local volume fraction.

As shown in Fig. 2.9b, the remote fractured TiB whiskers correspond to the low local volume fraction in network boundary and the abundant matrix tearing ridge lines indicate the large plastic zone at the tip of crack when the TiB whiskers crack. This can testify that the interpenetrating matrix structure can effectively constrain the crack propagation and reduce its speed, which is beneficial to the ductility of the composites. This is consistent with the superior elongation (15.4%) of the 5 vol.% TiBw/Ti composite. In contrast, as shown in Fig. 2.9d, a little matrix tearing ridge line and abundant ceramic fracture of TiB whisker and agglomeration correspond to the low ductility and high strength of the 12 vol.%TiBw/Ti composite. In addition, dimples can be easily formed around the dowel-like TiB whisker and constrained

![Fig. 2.9 SEM fractographs of 5 vol.% a, b and 12 vol.% c, d TiBw/Ti composites with a network microstructure at low a, c and high b, d magnification, respectively (Reprinted with the permission of Elsevier [2])](image-url)
by the neighboring TiB whisker, which demonstrate the toughening effect and strengthening effect of dowel-like whiskers.

### 2.3 Strengthening and Toughening Mechanisms of Network-Structured Composites

A simple model is built in order to better understand the effective strengthening and toughening mechanisms of the novel network microstructure as shown in Fig. 2.10a. At a higher level, the TiBw-rich network boundary is defined as Phase I, while the TiBw-lean center matrix region as Phase II. In that case, the present network microstructure is similar with the one with H–S upper bound as shown in Fig. 2.10b [3, 4]. For an isotropic two-phase composite, the H–S bounds for the elastic modulus ($E$) can be expressed as [3, 4]:

$$E_{HS-Upper}^{Upper} = \frac{E_r(E_rV_r + E_m(2 - V_r))}{E_mV_r + E_r(2 - V_r)}$$

$$E_{HS-Lower}^{Lower} = \frac{E_m(E_m(1 - V_r) + E_r(1 + V_r))}{E_r(1 - V_r) + E_m(1 + V_r)}$$

where $E_{HS-Upper}^{Upper}$ and $E_{HS-Lower}^{Lower}$ are the values of upper and lower bounds, respectively; $E_m$ and $E_r$ are the E values of the matrix and the reinforcement, respectively. $V_r$ is the overall volume fraction of the reinforcement. Assuming an ideal hard shell case, the spherical Ti matrix particle is encapsulated by hard TiB ceramic shell, which corresponds to the present network microstructure. The theoretical $E_1$ can be calculated by Eq. (2.8). But for another ideal case of the

![Fig. 2.10 A schematic illustration of the novel network microstructure (a) and Hashin–Shtrikman (H–S) bounds (b), gray area and white area present the reinforcing phase and matrix phase, respectively](image-url)
homogenous microstructure, i.e., the TiB reinforcement is homogeneously distributed in the matrix, which is equivalent to that the hard TiB ceramic phase is encapsulated by flexible Ti matrix. Therefore, the theoretical $E_2$ can be calculated by Eq. (2.9). Taking the $E$ values of 100 GPa for the pure Ti and 482 GPa for the TiB phase given in Gorsse’s paper [22], the TiB volume fraction of 8.5 vol.% into the Eqs. (2.8) and (2.9), the theoretical values of $E_1$ and $E_2$ are 130.1 and 122.4 GPa, respectively. In fact, the measured elastic modulus of the 8.5 vol.% TiBw/Ti composites with a network microstructure is 128.6 GPa, which is lower than the theoretical value (130.1 GPa). The reason is that the network boundary is not totally continuous. However, the measured elastic modulus of the 8.5 vol.% TiBw/Ti composites with a homogenous microstructure is 124.3 GPa, which is higher than the theoretical value (122.4 GPa). The reason is that the TiBw reinforcement is not totally discrete due to high volume fraction as shown in Fig. 2.5a. The whisker morphology (not particle) of TiB reinforcement is another factor for the higher modulus. However, the elastic modulus of the composites with a network microstructure is obvious higher than that of the composites with a homogenous microstructure. This phenomenon can be attributed to the higher contiguity of TiBw reinforcement due to the concentration distribution on the network boundary as shown in Fig. 2.5. That is to say, the TiBw/Ti composites with a network microstructure should exhibit a much higher strengthening effect, i.e., higher elastic modulus and higher strength, compared with the composites with a homogenous microstructure.

In other words, the present network microstructure can be viewed as bringing TiBw ceramic reinforcement into the grain boundary, which certainly further increase the “grain boundary strengthening effect”. At a lower level, the dowel-like TiBw and the in situ synthesized interface between TiBw and matrix can effectively connect the adjacent Ti particles. Additionally, the branched TiBw can further increase the strengthening effect by load transferring.

At a higher level, the network microstructure can bear higher strain, and the retained large TiBw-lean region can also bear higher strain and constrain the crack propagation. At a lower level, the interpenetrated network boundary can decrease the crack propagation speed [21]. Additionally, the dowel-like TiBw can stop the crack propagation, which is also beneficial to the ductility of the composites with a network microstructure.

2.4 Fabrication of (Ti$_5$Si$_3 +$ Ti$_2$C)/Ti Composites with Network Microstructure

Apart from TiB whiskers and TiC particles, SiC particles were usually selected as reinforcement of TMCs [6, 23, 24]. However, in the past 30 years, researchers have always been cautious and therefore done their best to restrict the reaction between the SiC reinforcement and Ti matrix [6, 23, 24]. In fact, as stated by Poletti [24], the
reactions between metal matrices and ceramic particles do not always imply a degradation of the mechanical properties. A thorough reaction may well be exploited for further improving the mechanical properties of TMCs. Additionally, the hybrid strengthening effect may also play a key role due to the different reaction products such as Ti₅Si₃ and Ti₂C. Moreover, the novel network microstructure might contribute to a superior combination of mechanical properties. Of particular interest is a low reinforcement volume fraction ranging from 1 to 5% [25].

A system of pure Ti and SiC was selected to fabricate the in situ composites due to their reaction capability [23, 24]. In order to tailor a novel network microstructure, large spherical pure Ti particles with an average particle size of 85 μm and fine polygonal SiC particles of 2 μm were selected as shown in Fig. 2.11. Before mixing, SiC particles were pretreated by acid cleaning and drying in order to remove impure elements such as S, O, and Ni on the particle surface [26]. Pure Ti particles and cleaned SiC particles were blended using low-energy milling at a low speed of 150 rpm for 5 h. The process was used to make the fine SiC particles adhere onto the large Ti particles without causing much deformation to the inherent shape of the Ti particles (Fig. 2.11c). Furthermore, this process can
be used to better exploit the toughening effect of the matrix and decrease processing time along with cost [2]. The blending processes were carried out in a pure argon atmosphere. The blended mixtures were hot pressed in vacuum (10^{-2} Pa) at 1200 °C under a pressure of 20 MPa for 60 min. Duda’s work indicated that Ti2C phase is easily formed when Ti is sufficient, while TiC phase is formed when C is rich [27]. Aksyonov et al. [28] also pointed out that the process of Ti2C formation is energetically favorable if TiC is in contact with titanium. Considering the designed network microstructure, only low volume fractions of reinforcements are permitted [10]. Therefore, the reaction between Ti and SiC is hypothetically described as follow [25]:

$$11Ti + 3SiC \rightarrow Ti_5Si_3 + 3Ti_2C$$ (2.10)

On the basis of the above equation, 1, 3, and 5 vol.% (Ti5Si3 + Ti2C)/Ti composites with a network microstructure were fabricated by controlling the added weight of the SiC raw material. For comparison, monolithic pure Ti sample was fabricated using the same processing parameters.

Figure 2.12 shows the X-ray diffraction pattern of the as-sintered 5 vol.% (Ti5Si3 + Ti2C)/Ti composite indicating that only Ti5Si3 and Ti2C phases exist in the as-sintered composite and no SiC phase and TiC phase are detected [25]. Similar results were also obtained for other composites. This result demonstrates that the in situ reaction between Ti and SiC was completed according to the hypothetical reaction in Eq. (2.10). Therefore, in situ hybrid (Ti5Si3 + Ti2C)/Ti composites were successfully fabricated.

Figure 2.13 shows the OM micrographs of the as-sintered (Ti5Si3 + Ti2C)/Ti composites with different volume fractions and that of the monolithic pure Ti. It is clear that, in the absence of Ti5Si3 and Ti2C reinforcements, the observed microstructure is the Widmanstätten microstructure (Fig. 2.13a), which is typically obtained when titanium is cooled slowly (furnace cooling) from above the β transus temperature. The size of the Widmanstätten microstructure is up to 600 μm which
is much larger than that of the as-received pure Ti powder (85 μm), which in turn indicates that the original pure Ti particles merged during the hot press sintering process. The new α phase was formed from the merged high temperature β phase. It is certain that the formation of large Widmanstätten microstructure is harmful to the mechanical properties of the pure Ti.

As seen from Fig. 2.13b, c, d, the composites are compacted with no visible pores. The synthesized reinforcements were distributed around Ti matrix particles forming a novel network microstructure.

The network structure can effectively constrain the matrix grain growth in each network unit. The size of network unit is similar with that of the as-received Ti particles. Moreover, several matrix grains form in individual network unit leading to significant refinement of the matrix grain itself. Therefore, the grain size of the as-sintered composites with a network microstructure is much smaller than that of the as-sintered monolithic pure Ti. Additionally, the local volume fractions of reinforcements on the network boundary increase with increasing the overall volume fractions from 1 to 5%. Moreover, some agglomerations formed in the 5 vol.% (Ti₅Si₃ + Ti₃C)/Ti composite due to high volume fraction (Fig. 2.13d), which is harmful to the composite ductility. In fact, the network microstructure can be viewed...
as that the reinforcements are introduced into grain boundary, which can effectively increase the grain boundary strengthening effect. It seems that the reinforcements are discretely distributed at grain boundary in the 1 vol.% (Ti5Si3 + Ti2C)/Ti composites, and then the continuity of reinforcements at grain boundary increases with increasing the reinforcement volume fractions. For the discrete distribution of reinforcements in the 1 vol.% (Ti5Si3 + Ti2C)/Ti composites, the continuity can be viewed as 0, while as 1 for the total agglomerations. An appropriate continuity can exploit a superior strength along with an appropriate ductility (3 vol.% in the present system), while a much high continuity (such as 1) will weaken the composites due to very low ductility.

Figure 2.14 shows the SEM micrograph and the results of energy dispersive spectroscopy (EDS). It can be clearly seen that there are two different morphologies of reinforcements, equiaxed particle and short rods. Compared with the XRD result, the equiaxed particle should be the Ti2C phase. Formation of the equiaxed morphology is due to the face-centered cubic structure of Ti2C phase. Correspondingly, the rod-like reinforcement should be Ti5Si3 phase. Because of its complex hexagonal D88 structure, the Ti5Si3 phase easily grows to rod-like morphology. In addition, the several equiaxed matrix grains in single network unit can be clearly seen. Therefore, the matrix grain size is effectively refined due to the existence of network-structured distribution of reinforcements [13].

Figure 2.15 shows stress–strain curves of the as-sintered monolithic pure Ti and the in situ (Ti5Si3 + Ti2C)/Ti composites. Table 2.2 summarizes their tensile properties in order to further assess the contribution of network microstructure and the in situ hybrid Ti5Si3 and Ti2C reinforcements synthesized by the completed

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**Fig. 2.14** SEM morphology and EDS results of 5 vol.% (Ti5Si3 + Ti2C)/Ti composite with a novel network microstructure. a SEM micrograph, b EDS result of point A, c EDS result of point B (Reprinted with the permission of Elsevier [25])
Combining Fig. 2.15 and Table 2.2, the tensile yield strength ($\sigma_{0.2}$) of the novel network-structured composites increased from 436 MPa to 668 MPa, 789 MPa and 846 MPa, respectively, by adding 1, 3, and 5 vol.% reinforcements. That is to say, the $\sigma_{0.2}$ of the composites is increased by 53.2%, 81.0%, and 94.0% relative to that of the monolithic pure Ti, respectively. It is likely that this is the most effective strengthening effect reported to date, considering only less than 5 vol.% reinforcements have been introduced. According to the above observations and previous work [2, 13, 21], the superior strengthening effect can be attributed to the formation of network microstructure, matrix grain refinement, and the synthesis of in situ hybrid reinforcements. The reinforcement distribution along grain boundary forming the network microstructure can effectively increase the grain boundary strengthening effect by increasing dislocation accumulation density during the matrix tensile deformation process. Moreover, the hybrid reinforcements can exploit a superior hybrid strengthening effect [29]. Moreover, the ultimate tensile strength ($\sigma_b$) was increased from 530 MPa to 852 MPa, 868 MPa, and 858 MPa, an increase by 60.8%, 63.8%, and 61.9%, respectively. By comparison,
the ultimate strength of the composite is as good as that (855 MPa) of Ti6Al4 V alloys [21] by adding as low as 1 vol.% reinforcement.

In the case of tensile elongation, it is incredible that the measured elongation of the 1 vol.%(Ti5Si3 + Ti2C)/Ti composite is much higher than that of the pure Ti, i.e., the elongation is increased by 68.0% from 17.2% to 28.9%. While it is normal that the pure Ti with tensile strength of 530 MPa exhibits an elongation of 17.2%, the 1 vol.%(Ti5Si3 + Ti2C)/Ti composite exhibits an elongation of 28.9% is exceptional, given the fact that, in our previous work, the elongation of a TiBw/Ti6Al4 V composite with a network microstructure decreased from 11.3 to 9.2% by adding 2 vol.% TiB whisker reinforcement [21]. Combining microstructural observations and mechanical analysis, the superior tensile elongation of the novel composite with low reinforcement volume fraction can be attributed to the following factors [25]: (1) the tailored network microstructure can improve the ductility of the composites by changing the deformation mechanism [21]; (2) the in situ reaction can improve the interface bonding between reinforcement and matrix; (3) the in situ hybrid reinforcements are positive to the ductility of the composites [29]; (4) the matrix grain refinement due to the existence of network reinforcement can effectively improve the matrix ductility; (5) the large size matrix region can bear large strain and decrease speed of crack propagation; (6) the dispersed reinforcements can effectively pin dislocation, which can exploit a superior ductility and strain hardening effect. This statement can also be verified by the tensile stress–strain curve of the 1 vol.%(Ti5Si3 + Ti2C)/Ti composites with a much high ultimate strength.

However, the tensile elongation sharply decreases from 28.9 to 6.58% and then 1.53% with increasing volume fractions from 1 to 3 vol.% and then 5 vol.%. This sharp decrease of the tensile elongation is attributed to the reinforcements, especially the rod-like Ti5Si3 phase that are concentrated on the network boundary, which effectively increases the local reinforcement volume fraction (the reinforcement continuity) on the network boundary [21]. In particular, the agglomeration formation in the 5 vol.%(Ti5Si3 + Ti2C)/Ti composite plays a key role decreasing the ductility (Fig. 2.13d). This is also the reason that the tensile yield strength increased with increasing reinforcement volume fractions. Nevertheless, the elongations of 6.58 and 1.53% are pretty high considering the tensile yield strength enhancements of 81% and 94%, for the as-sintered composites fabricated by powder metallurgy. It is certain that both tensile elongation and strength can be improved by subsequent deformation, such as rolling or extrusion.

Table 2.2 also shows the high-temperature tensile strength of the prepared composites, which indicates a high strengthening effect at high temperatures for the novel composites with a network microstructure. It can be clearly seen that the tensile strength of the composites increases with increasing reinforcement volume fractions, and decreases with increasing testing temperatures. The superior strengthening effect at high temperatures can be attributed to the reinforcement network distribution around matrix particles which is analogue to the grain boundary strengthening effect.
Figure 2.16 shows the fracture surfaces of the prepared composites with different reinforcement volume fractions at different magnifications [25]. As shown in Fig. 2.16a, tearing ridge lines and dimples can be found almost everywhere, while very little ceramic reinforcement cracks can be found. This is due to the low reinforcement volume fraction of 1 vol.%. Additionally, the tearing ridge lines are short and the dimples are small, which can be attributed to matrix grain refinement. This observation is consistent with the superior tensile elongation. As shown in Fig. 2.16b, c, the tearing ridge lines and dimples decrease, with corresponding increase in ceramic reinforcement cracks as the reinforcement volume fraction increases. In particular for the 5 vol.% (Ti₅Si₃ + Ti₂C)/Ti composite, the crack propagates along the network boundary as shown in Fig. 2.16c, which can sufficiently exploit the reinforcement strengthening effect [21], however, this constrains the toughening effect of large Ti matrix particles. Therefore, the 5 vol.% (Ti₅Si₃ + Ti₂C)/Ti composite exhibits a superior tensile strength improvement of 94%, but a low tensile elongation. That is to say, the network-structured reinforcements can effectively strengthen the composites by increasing dislocation accumulation density at grain boundary, while the dispersed reinforcements at grain
boundary can effectively enhance the ductility by pinning dislocation. Furthermore, the grain refinement due to the network microstructure can improve both the strength and the ductility of the composites.

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