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Investigation on strengthening and toughening mechanisms of Nb-Ti-ZrB$_2$ metal matrix ceramic composites reinforced with in situ niobium and titanium boride

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Abstract

Nb-Ti-ZrB$_2$ metal matrix ceramic composites with a fixed atomic ratio Nb/Ti=2/1 and ZrB$_2$ volume fraction changing from 0, 11vol.%, 23vol.% to 36vol.% were hot pressed at 1600℃ under 30MPa. The influence of ZrB$_2$ content and Ti addition on the phase constitution, microstructure evolution, toughening mechanisms and strengthening mechanisms were investigated. It was shown that the formation of in situ Nb-rich (Ti,Nb)B and Ti-rich (Nb,Ti)B was attributed to a high mutual solubility of monoborides and the amount of niobium and titanium borides increased with increasing ZrB$_2$ content. The needle-shaped (Ti,Nb)B phase weakened the damage to fracture toughness caused by ZrB$_2$ particle fracture due to crack bridging, crack defection and the pull-out toughening mechanisms. The highest fracture

toughness of the Nb-Ti-ZrB$_2$ composites was 12.0 MPa·m$^{1/2}$. The stiff (Nb,Ti)B phase acted as a strong obstacle to the dislocation motion, leading to dislocation pile-up and enhancing the strength of the Nb-Ti-ZrB$_2$ composites during compression tests. However, stress concentration around the needle-shaped (Ti,Nb)B phase easily leads to crack initiation and extension, resulting in decreased strength. The yield strength of Nb-Ti-ZrB$_2$ composites ranged from 657.3 MPa to 1783.0 MPa owing to the combined influence of the strenghening mechanism caused by (Nb,Ti)B and the weakening mechanism caused by (Ti,Nb)B. The compressive deformation and failure process were also discussed in detail in this study.

Keywords: Hot-pressing; Nb-based composite; ZrB$_2$; Mechanical properties; Fracture behavior

1. Introduction

Nb alloys are the most potential high temperature structural materials due to their high melting point, good corrosion resistance and excellent refractory properties [1-3]. However, the main obstacles for them to be used widely is their low fracture toughness at room temperature. To overcome this drawback, various approaches have been used. The effect of W [4], Ta [5] and V [6] on toughening mechanism of Nb or Nb-Si alloys were investigated. Fracture toughness of the Nb-Si based alloys were improved by the addition of Ta, but reduced to 8.2 MPa·m$^{1/2}$ by addition of W. Nb$_{SS}$/Nb$_3$Al [7] and Nb$_{SS}$ /Nb$_5$Si$_3$ [8] were fabricated to study the effect of intermetallic compounds on the strength and toughness. A ductile/reinforcement two-phase structure is formed in the Nb$_{SS}$/Nb$_5$Si$_3$ composite. Nb$_5$Si$_3$ phases are the reinforcement phases which are beneficial to room temperature strength and oxidation resistance. The Nbss phase is the ductile matrix which can enhance fracture toughness and room temperature ductility [8]. However, the fracture toughness and ductility of these composites are still too low to be used

in the industry [9].

Particulate reinforced metal matrix composites (PRMMCs) are being considered as potential materials for aerospace owing to their high wear resistance, good balance between strength and toughness, and low thermal expansion [10]. Moreover, the PRMMCs can be fabricated with near isotropic properties in three orthogonal directions compared with the fiber or filament reinforced composites [11]. Many studies have focused on metal matrix composites reinforced with Nb particles [12, 13], but there haven't been any reports on the ceramic particulate reinforced Nb based composites. In previous studies of our team, he (0-60 vol%) ZrB_2 particles reinforced NbMoss solid solution matrix composites were fabricated by hot-press sintering at 2400°C [14, 15]. The experimental results show that the ZrB_2 ceramic particles can significantly improve the compressive strength of the NbMoss matrix. The highest compressive strength at room temperature reached 1635.91 MPa, and the strength at 1300 °C is still over 700 MPa. However, their room temperature fracture toughness is only 3.99-6.34 MPa·m$^{1/2}$, restricting their practical application. It is necessary to adjust the chemical element composition to obtain a good ductility and a high fracture toughness of the ZrB_2 particles reinforced Nbss composite when maintaining its high compressive strength.

One of the most promising approaches to enhance the fracture toughness of particulate reinforced Nb composites is to weaken the negative effect of the ceramic reinforcement brittleness fracture by crack deflection and crack bridges provided by a ductile metal matrix [16, 17]. It has been demonstrated that the addition of Ti can improve the ductility of the Nb [18, 19]. The fracture toughness of Nb-15Al-Ti alloys increases from 27 MPa·m$^{1/2}$ to 102 MPa·m$^{1/2}$ while Ti content increases from 10 at.% to 40 at.% due to the effects of TiO_2-induced closure

[20]. Consequently, ZrB_2 was selected as the reinforced particles and Ti was added into Nb to form the NbTiss solid solution matrix to provide toughness and ductility in this work. As for the processing techniques, hot pressing is a more feasible method for processing refractory Nb-based composites with finer microstructures and better compositional homogeneity than vacuum arc melting or casting [11, 21]. During hot-press sintering, the ZrB_2 particles have the possibility of decomposing into Zr and B and then B can react with Nb and Ti to form the in-situ NbB and/or TiB. According to the study of D. B. Borisov et al [22], the phase composition of the Nb-Ti-B alloy is composed of three phase NbTiss+NbB+TiB when the Nb/Ti is approximately 2/1 (atomic ratio). NbB and TiB are also excellent reinforced particles to Nb alloys due to the combination of high specific strength and high temperature resistance [23]. In this study, the atomic ratio of Nb/Ti was chosen as 2/1 and Nb-Ti-$xZrB_2$ (x=0, 11, 23, 36vol.%) composites were hot pressed at 1600℃ under 30 MPa. The phase composition and microstructures evolution were investigated. The compressive yield strength, fracture toughness and fracture morphologies were examined and the related strengthening mechanism and toughening mechanism were discussed in detail.

2. Materials and Methods

2.1 Samples fabrication

The raw materials are ZrB_2 (23μm, purity>99.95%), Nb (18-25μm, purity> 99.95%) and Ti (45μm, purity> 99.95%) powders provided by Beijing gold crown new material Technology Co., Ltd. China. Four powder mixtures (Table 1) with different ZrB_2 volume fraction were mixed and pulverized in a planetary ball mill in ethanol for 12 h at a speed of 200 rpm. Then the mixtures were dried at 110 °C for 3 h and uniaxially cold-pressed into platelets under a pressure

of 10 MPa. Subsequently, the platelet was put into a carbon die with BN coating in a vacuum hot press furnace and the hot-press sintering process started. At the first stage of the sintering process, the heating rate was $10°C\ min^{-1}$ and vacuum degree was ~1.5 Pa. The first dwell isotherm was 10 min at 400°C. The volatile species in the sample could be removed during this stage. At the second stage, the heating rate was $20°C\ min^{-1}$ and vacuum degree was ~0.2 Pa. The second dwell isotherm was 2 h at 1600°C and a pressure of 30 MPa was supplied during the dwell time. In the end, the compact was naturally cooled down in the hot press furnace. One billet, with dimensions of $36×25×20\ mm^{3}$, was prepared for each experiment.

Table 1 Raw materials compositions

Sample	Atomic ratio			ZrB_2 volume fraction (%)
	ZrB_2	Nb	Ti	
Z0	—	2	1	0
Z1	0.4	2	1	11
Z2	0.9	2	1	23
Z3	1.7	2	1	36

2.2 Mechanical property evaluation

Fracture toughness test specimens with dimensions of 3mm×4mm×36mm were prepared from the hot-pressed compacts by electro-discharge machining and the notch at mid-length was 0.1 mm wide and 0.6 mm deep according to GB/T 23806-2009. Compression test specimens of 10mm in height and 10mm in diameter were also prepared according to GB/T 7314-2005. SiC sandpapers from #100 to #800 were used to grind the specimens. The fracture toughness value was determined by a three point bending test using the single-edge-notched beam (SENB) specimens by an Electromechanical Universal Testing Machine (C45.105). The surfaces obtained from the Indentation Method (IM) were also investigated to show the crack propagation pathways. The final result is the average of five specimens. The compression tests

were conducted on a hydraulic universal machine (SHT 4305) operating under a load control of

600 N/s. The loading direction was set to be perpendicular to the hot-pressing direction.

2.3 Microstructure characterization

The phase identification was performed on bulk samples using a Rigaku D/max-rA X-ray

diffract meter with Cu $K\alpha$ radiation, between 2θ angles of 10° and 90° at a scanning rate of

8°/min. The microstructures were examined on a FESEM scanning electron microscope

(ZEISS SUPRA-55) equipped with an EDAX genesis xm-2 X-ray spectrometer. The surfaces

of specimens for Vickers hardness, X-ray diffraction analysis and microstructure observation

were grinded and polished.

3. Result

3.1 Phase and microstructure

XRD patterns of the Nb-Ti-ZrB$_2$ composites are displayed in Fig. 1. Peaks from the

(Ti,Nb,Zr)ss, TiB, NbB and ZrB$_2$ phases are detected. The intensity of the nionium boride

peaks increases with increasing ZrB$_2$ volume fraction in the corresponding XRD profiles,

indicating the amount of TiB and NbB phases increases. For Z1, Z2, Z3 samples, the

formation of the β(Ti,Nb,Zr)ss solid solution is mainly due to the solution of Ti and Zr atoms

into a Nb crystal lattice. It should be noted that the concentration of Ti is ~22.28 at.% for NbB

and the concentration of Nb is ~24.88 at.% for TiB, indicating the existence of Ti-rich

(Nb,Ti)B and Nb-rich (Ti,Nb)B (see Table 2 for details). (Nb,Ti)B and (Ti,Nb)B phases are

also found in the annealed Ti-Nb-B alloys by D. B. Borisov [22]. In his study, the solubility of

Nb in TiB is up to 23 at.% and the highest solubility of Ti in NbB is 15 at.%. Ding et al. [24]

found that only the single β(Ti,Nb)ss phase appeared in the Nb-based alloy when the addition

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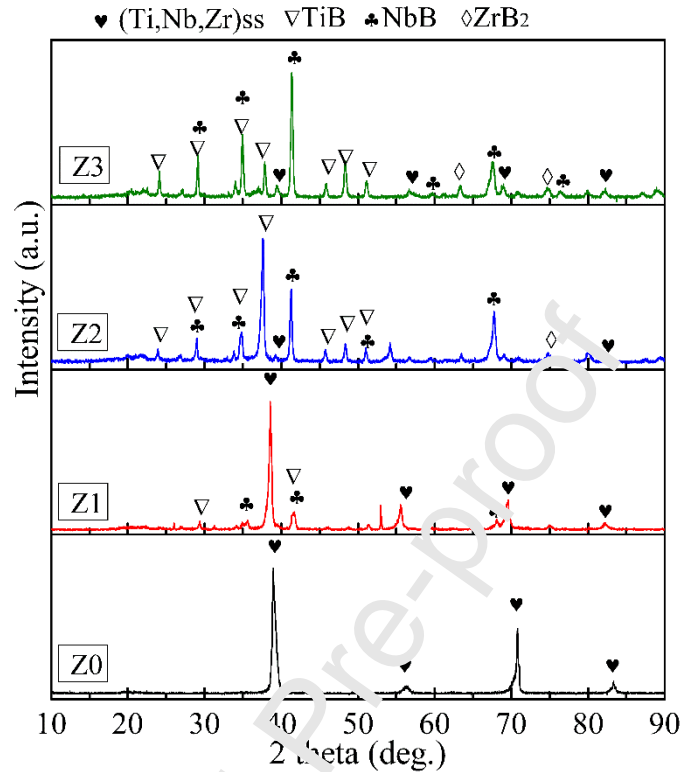of Ti was less than 35 at.%. This is the reason why only the β(Ti,Nb)ss phase is detected in Z0.

Fig. 1. XRD patterns for Nb-Ti-ZrB$_2$ composites after hot-press sintering at 1600°C.

The microstructure and EDX results of the β(Ti,Nb,Zr)ss, Ti-rich (Nb,Ti)B, Nb-rich (Ti,Nb)B and ZrB$_2$ phases in Z1-Z3 are shown in Fig. 2 and Table 2. Arrows Ai, Bi, Ci and Di (i=1, 2, 3) indicate different phases with different atmotic compositions. Phase Ai is the (Nb,Ti,Zr)ss solid solution phase containing Nb, Ti, Zr and B without a stoichiometric composition. Phase Bi is the Nb-rich (Ti,Nb)B phase with a stoichiometric composition quite close to TiB and the concentration of Nb in Z1, Z2 and Z3 is 21.64 at.%, 24.88 at.% and 17.01 at.%, as indicated by arrows B1, B2 and B3, respectively. Phase Ci is the Ti-rich (Nb,Ti)B phase containing 18.18 at.%, 22.28 at.% and 17.92 at.% Ti, as indicated by arrows C1, C2 and C3, respectively. The high solubility of Ti in NbB (~30 at.%) and of Nb in TiB (~23 at.%) has also been observed by G. V. Samsonov et al. before [22, 25, 26]. ZrB$_2$ is detected in Z2 and Z3

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according to XRD patterns; however, the SEM image and EDX analysis show that only Z3 exhibits large residual ZrB_2 particles, as indicated by D3. The amount of ZrB_2 in Z2 is too small to be distinguished by a scanning electron microscope due to its the limited resolution. In general, the EDX element analysis is consistent with the phase constitution identified by the XRD patterns.

Fig. 2 shows the typical images of the polished $Nb-Ti-ZrB_2$ composites. The needle-shaped $(Ti,Nb)B$ [23], the nearly spherical NbB [22] and the polygonal shaped ZrB_2 [14] are displayed in the $(Ti,Nb,Zr)ss$ solid solution matrix. During the hot-pressing process, the ZrB_2 particles firstly decompose into Zr and B, and then B reacts with Ti by an in situ chemical reaction $Ti+B=TiB$ to precipitate an intermetallic TiB phase [27]. TiB phase usually grows along the [010] direction and presents a needle-shaped or rod-like morphology due to its B27 crystal structure [23, 28]. The formation of $\beta(Ti,Nb,Zr)ss$ and NbB phases is due to the eutectic reaction $L \leftrightarrow Nbss + NbB$ [29], and the formation of $(Ti,Nb)B$ and $(Nb,Ti)B$ is due to the high mutual solubility of NbB and TiB [23]. However, the decomposition of ZrB_2 is incomplete as there are residual polygonal-shaped ZrB_2 particles distributed in the $(Ti,Nb,Zr)ss$ matrix of Z3 (Fig. 2c and c1). Moreover, with increasing ZrB_2 content in the raw material, more and more $(Ti,Nb)B$ whiskers are synthesized through the above chemical reaction, then the resulting $(Ti,Nb)B$ grows and connects rapidly to form the $(Ti,Nb)B$ cluster (Fig. 2a-c). The amount of $(Ti,Nb)B$ cluster increases with increasing ZrB_2 volume fraction in the raw material. Both the $(Ti,Nb)B$ cluster and the polygonal ZrB_2 can cause stress concentration, causing a negative influence on the compressive properties of the investigated $Nb-Ti-ZrB_2$ composites, which will be discussed in section 4.2.
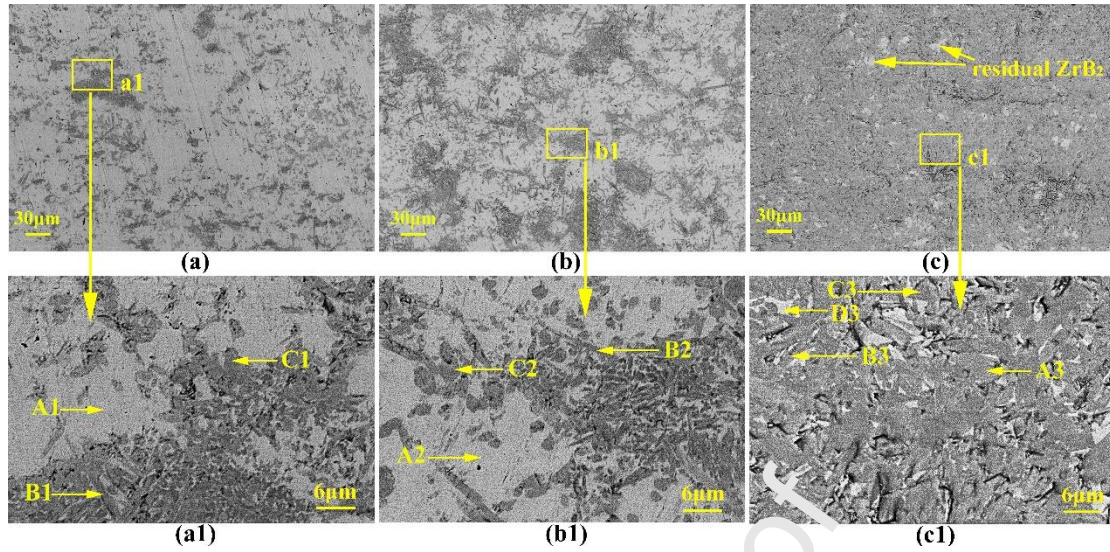
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Fig. 2. Microstructure of Nb-Ti-ZrB$_2$ composites: (a)Z1, (b)Z2 (c)Z3, (a1)Magnification of Z1, (b1)Magnification of Z2, (c1)Magnification of Z3

Table 2 EDS results for the typical phases in Fig 2

Sample	Arrow	Composition（at.%）				Constituent phases
		Nb	Ti	Zr	B	
	A1	29.05	35.15	6.86	28.94	(Nb,Ti,Zr)ss
Z1	B1	21.64	25.34	4.83	48.18	Nb-rich (Ti,Nb)B
	C1	28.79	18.18	1.79	51.25	Ti-rich (Nb,Ti)B
	A2	24.09	21.19	17.26	37.46	(Nb,Ti,Zr)ss
Z2	B2	24.88	24.74	4.66	45.71	Nb-rich (Ti,Nb)B
	C2	26.03	22.28	6.42	45.26	Ti-rich (Nb,Ti)B
	A3	13.30	14.43	33.53	38.73	(Nb,Ti,Zr)ss
Z3	B3	17.01	24.19	10.12	48.68	Nb-rich (Ti,Nb)B
	C3	22.48	17.92	6.92	52.68	Ti-rich (Nb,Ti)B
	D3	2.35	3.50	38.44	55.71	ZrB$_2$

3.2 Fracture toughness

The fitting curve of fracture toughness versus ZrB$_2$ volume fraction for the Nb-Ti-ZrB$_2$ composites is shown in Fig. 3. It can be seen that the addition of ZrB$_2$ particles decreases fracture toughness of Nb-Ti alloys compared to Z1-Z3 with Z0. The addition of ceramic particles to alloys causing a decrease in fracture toughness is also observed in other PMMCs such as Al$_2$O$_3$/SiC/TiB$_2$ reinforced Al/Ti matrix composites. This phenomenon is due to the

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restrained plastic deformation of the matrix caused by the stiff particles [30] and particle fracture, particle clustering, and particle/matrix debonding [31, 32]. Rice and Johnson [33] indicate that the toughness should decrease as a function of the particulate volume fraction to the power -1/6. This is substantiated by the present results, as shown in Fig. 3 and Table 3. However, the fracture toughness of Z2 is an exception to the Rice and Johnson rule. This phenomenon is mainly due to three toughening mechanisms caused by the needle-shaped (Ti,Nb)B phase, which will be discussed in detail in section 4.1
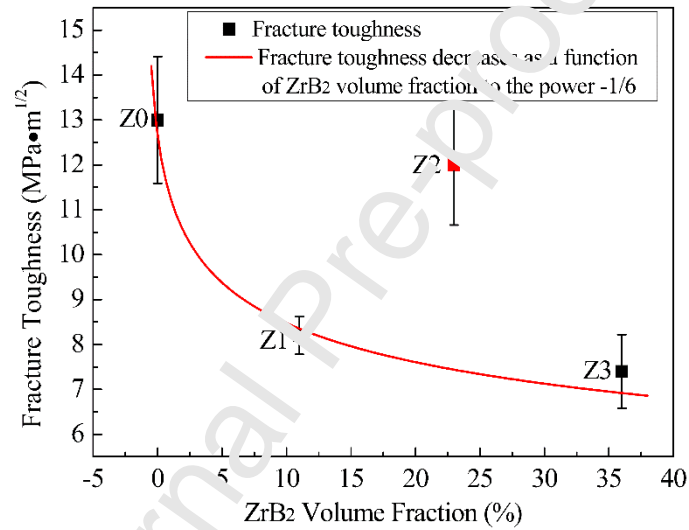
Fig. 3. Fitting curve of fracture toughness versus ZrB_2 volume fraction for the Nb-Ti-ZrB_2 composites.

Table 3 Mechanical properties of Nb-Ti-(ZrB_2) composites

Sample	Fracture toughness $(MPa \cdot m^{1/2})$	Yield strength (MPa)
Z0	13.0±1.4	1252.7±70.4
Z1	8.2±0.4	1785.6±116.3
Z2	12.0±1.3	1461.4±49.6
Z3	7.4±0.8	805.1±30.9

3.3 Compressive properties

The true compressive stress-strain curves of the Nb-Ti-ZrB_2 composites are shown in Fig. 4

and Table 3 summarizes their compressive yield strength at 0.2% plastic compressive strain. It can be seen that Z1-Z3 experience brittleness deformation while Z0 displays plastic deformation with good ductility. Generally, the addition of ZrB_2 ceramic particles into an Nb-Ti alloy matrix can improve yield strength of Nb-Ti-ZrB_2 composites. This phenomenon is due to the secondary phase strengthening mechanism, which can be described as $\Delta\sigma = V_p\sigma_m\left[\frac{(l+t)A}{4l}\right]$ [34, 35], where the yield stress increment $\Delta\sigma$ is proportional to matrix yield stress σ_m and particulates volume fraction V_P. $\left[\frac{(l+t)A}{4l}\right]$ is a constant related to the size and thickness of the particulate. According to the above equation, the yield stress increment ($\Delta\sigma$) increases with increasing hard particulates. The secondary phase strengthening mechanism has also been confirmed in the other Nb-based composites, such as Nb-Mo-ZrC [36] and Nb-Ti-C-B [37] composites. However, in this study, the yield strength of Nb-Ti-ZrB_2 composites decreases with increasing ZrB_2 particles, although the amount of stiffening secondary phase Ti-rich (Nb,Ti)B and Nb-rich (Ti,Nb)B increases with increasing ZrB_2 particles (Fig. 5). This phenomenon is mainly due to the stress concentration around the needle-shaped (Ti, Nb)B phases and the large residual ZrB_2 particles. The detailed weakening mechanism and the deformation behavior of Nb-Ti-ZrB_2 composites will be discussed in section 4.2.
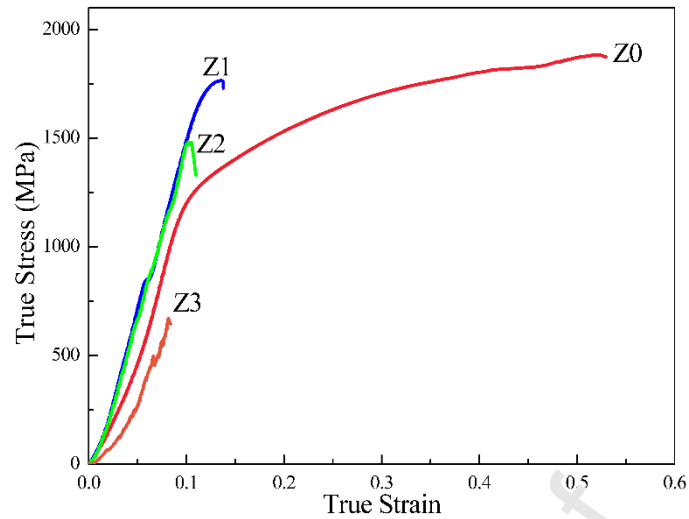
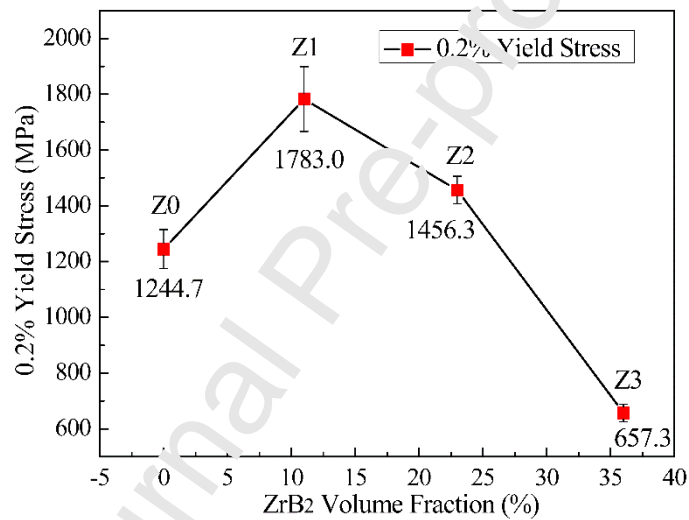Fig. 4. True stress-strain curves for Nb-Ti-(ZrB$_2$) composites.

Fig. 5. 0.2% Yield strength of Nb-Ti-ZrB$_2$ composites.

4. Discussion

4.1 Toughening mechanism and fractography

The deformation behavior of Nb-Ti-ZrB$_2$ composites is different from that of ductile alloys and brittle ceramics [38]. To explore the toughening mechanisms of Nb-Ti-ZrB$_2$ composites, the paths of Vickers-identification-caused cracks of Z2 and Z3 were observed on Fig. 6. As shown in Fig. 6c and d, the crack bridging and deflection occurs around the needle-shaped (Ti,Nb)B phases. The difference in elastic modulus between the (Ti,Nb)B phase and the β(Ti,Nb,Zr)ss

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solid solution phase leads to the interaction between phase boundaries and crack tips, resulting in the tortuous pathway of the crack propagation (Fig. 6a). Once the cracks have reached the interfaces between the stiff (Ti,Nb)B reinforced phase and ductile β(Ti,Nb,Zr)ss matrix, the different crack-tip opening displacement between the brittle reinforcement and the ductile matrix leads to the crack bluntness and circumvention around the stiff (Ti,Nb)B phase. Consequently, the higher (Ti,Nb)B content results in a higher possibility of crack bridging and deflection.

Crack bridging and deflection can reduce the crack-tip stress intensity factor and cause energy dissipation, which is beneficial for toughening brittle materials [18, 39]. However, the crack was across the big residual ZrB_2 particles directly in Z3 (Fig. 6d), indicating the big residual ZrB_2 particle in the crack propagation path had a negative effect on crack bridging and deflection. This phenomenon is also observed on the study of SiC-ZrB_2 composites reported by Guo et al. [40]. In their study, the crack deflection and bridging appeared only at the small stiff SiC particles rather than the large ones. Therefore, the reason for the low fracture toughness of Z3 with higher (Ti,Nb)B content when compared with Z2 is the existence of the big residual ZrB_2 particles, which makes cracks cross directly rather than bridge or deflect.
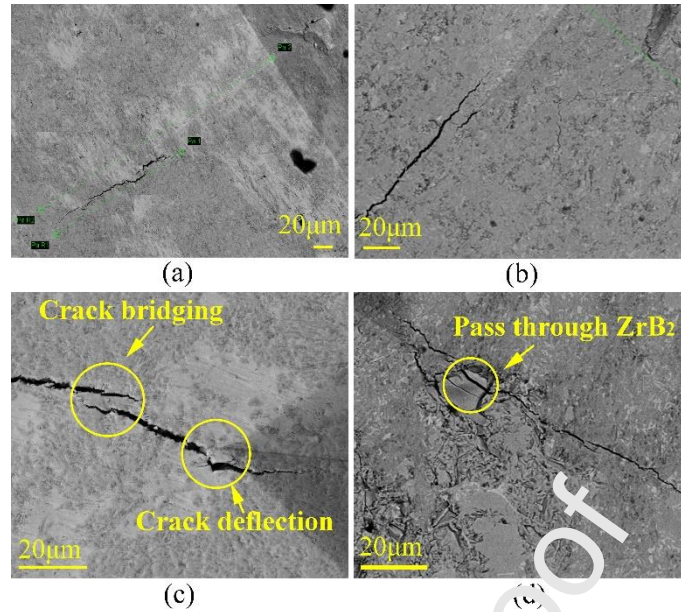
Fig. 6. Crack propagation pathways of Nb-Ti-ZrB$_2$ composites: (a)Z2, (b)Z3, (c)high magnification of Z2, (d)high magnification of Z3.

The fracture surfaces of Nb-Ti-ZrB$_2$ composites are shown in Fig. 7. Three different fracture modes were observed in Fig. 7: quasi-cleavage of the (Ti,Nb,Zr)ss, cleavage of the (Nb,Ti)B, and pull-out of the (Ti,Nb)B. Quasi-cleavage fracture occurred in the (Ti,Nb,Zr)ss solid solution matrix with obvious river patterns [41, 42]. Cleavage fracture takes place in the grains of (Nb,Ti)B with rough cleavage planes and the transgranular fracture surfaces. Pull-out of the needle-shaped (Ti,Nb)B on the crack surface of Z2 is positive for crack bridging [42], which is in agreement with the crack path propagation shown in Fig. 6c. The fine and needle-shaped (Ti,Nb)B phase results in more grain boundaries to hinder the crack propagation, and the pull-out of (Ti,Nb)B phases absorbs much of the crack expansion energy [28]. The microcracks and deflects in the Nb-Ti-ZrB$_2$ composites were initiated and expanded under the external loading, and finally fractured with obvious river patterns around the stiff phases. This fracture process is reasonably speculated from the fracture surfaces shown in Fig. 7. Rising R-curves

would be generated, which is consistent with these fracture surfaces [43, 44]. Related research about the influence of phase composition and microstructure on the shape of R-curves will be conducted in the future.

In general, there is no doubt that the addition of ZrB_2 particles causes the decrease in fracture toughness of Nb-Ti-ZrB_2 composites due to the restrained plastic deformation of the matrix and the brittle transgranular fracture of ZrB_2. However, the (Ti,Nb)B phase is beneficial to fracture toughness due to crack bridging, crack defection and the pull-out toughening mechanism. The increase of fracture toughness caused by (Ti,Nb)B in Z2 exceeds the decrease in fracture toughness caused by the ZrB_2 fracture. That is the reason for the high fracture toughness of Z2. Toughening mechanisms of the (Ti,Nb)B phase can be described schematically, as shown in Fig. 8.
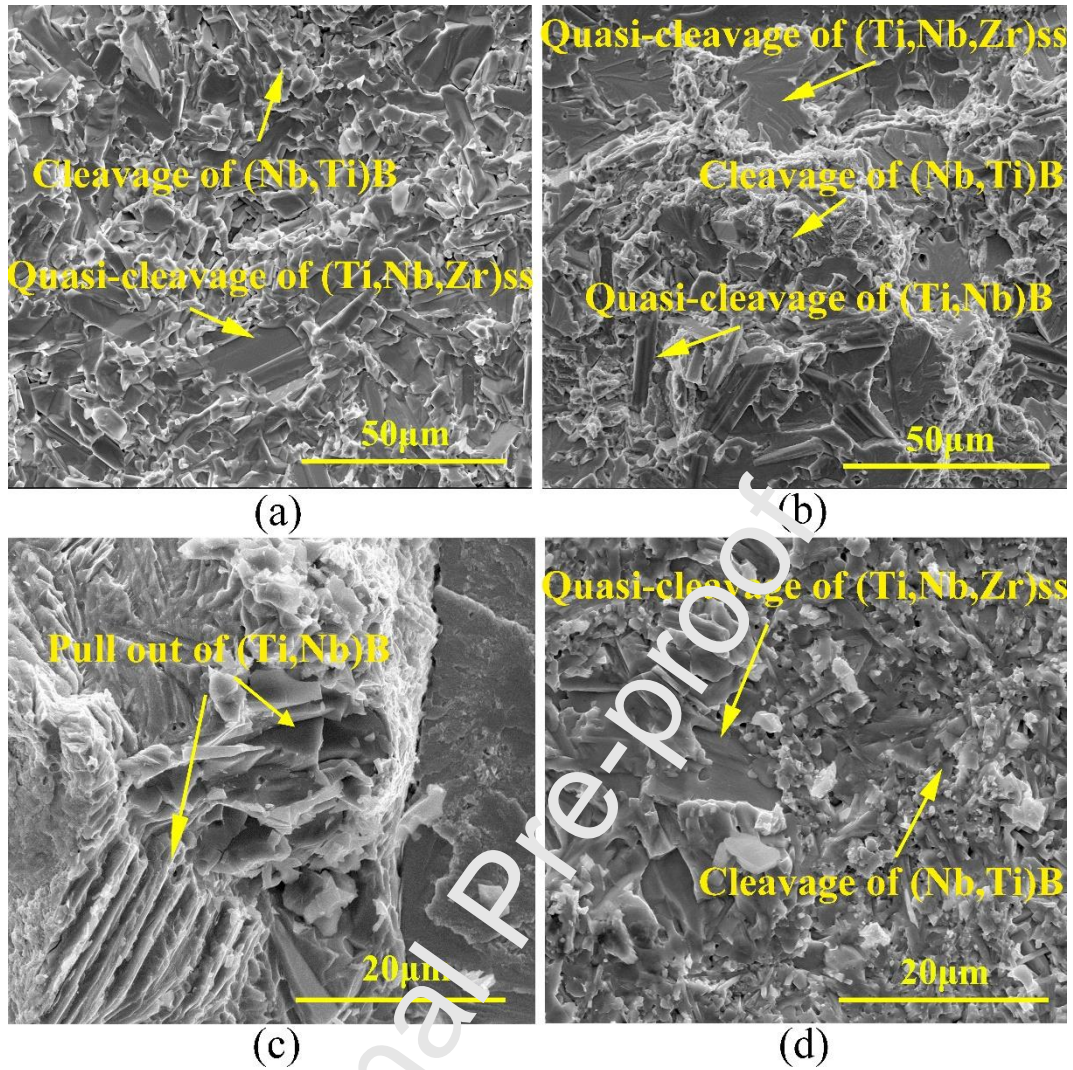
Fig. 7. Fracture surface of Nb-Ti-ZrB$_2$ composites: (a)Z1, (b)Z2, (c)high magnification of Z2, (d)Z3.

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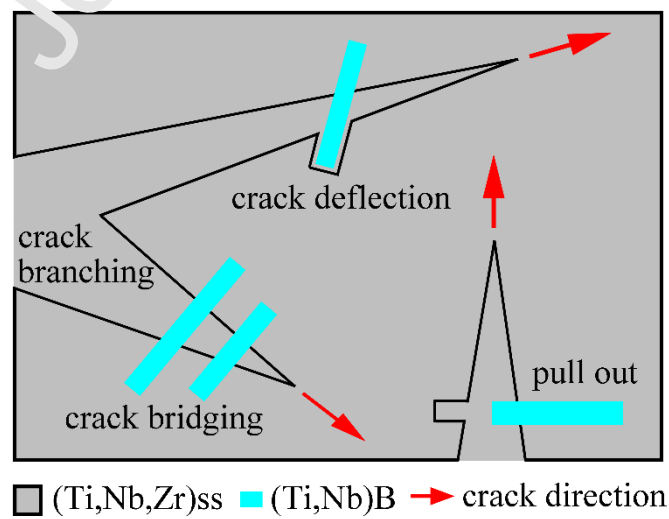
Fig. 8. Schematic diagram of toughening mechanisms of (Ti,Nb)B phase.

4.2 Strengthening mechanism and failure process

As shown in Fig. 1 and Fig. 2, there are three different hard phases: (Nb,Ti)B, (Ti, Nb)B and residual ZrB_2 particles distributed in the plastic (Ti,Nb,Zr)ss solid solution matrix in the Nb-Ti-ZrB_2 composites. During compression tests, the (Nb,Ti)B stiffening phase was a strong obstacle for the dislocation motion. The dislocations were piled up around the (Nb,Ti)B phase, which is benefical to the improvement of the strength of Nb-Ti-ZrB_2 composites. The strengthening effect caused by the (Nb,Ti)B phase is also reported by X.J. Zhang et al [45]. However, there are two negative factors caused by the existence of the needle-shaped (Ti, Nb)B phase and the big residual ZrB_2 particles, which do harm to the compressive strength in the investigated Nb-Ti-ZrB_2 composites. First, the stress concentration around the needle-shaped (Ti, Nb)B phase easily leads to crack initiation and propagation with less compatible deformation, resulting in decreased strength during composite deformation [46]. It has been proved that the adhesion strength between the needle-shaped (Ti,Nb)B phase inside the (Ti,Nb)B clusters is weak, which means that it is easy for the (Ti,Nb)B phase to break and separate from the matrix in the (Ti,Nb)B cluster [46, 47]. Therefore, the (Ti,Nb)B clusters promote crack initiation and propagation and weaken the strength of the investigated Nb-Ti-ZrB_2 composites. The content of (Ti,Nb)B clusters increases with increasing ZrB_2 volume fraction, resulting in a decreased compressive yield strength. Second, the large residual ZrB_2 particles lead to fewer boundaries to absorb strain energy, and the stress concentration caused by their polygonal shape microstructures also results in the greater possibility of crack initiation and propagation [14]. Therefore, the strength of the Nb-Ti-ZrB_2 composites depends

on the combined influence of the strenghening mechanism caused by (Nb,Ti)B and the weakening mechanism caused by (Ti,Nb)B and ZrB_2. As shown in Fig.5, it is obvious that the weakening mechanism exceeds the strengthening mechanism, resulting in a decrease in compressive yield strength.

The compressive fracture surfaces of Nb-Ti-ZrB_2 composites are shown in Fig. 9a-c. The stone-like, terrace-type and river pattern morphologies are observed. Large cleavage planes and cleavage steps are also observed and the cleaved cracks propagate along the cleavage plane [48]. Fig. 10a-c show the failure morphoologies of the Nb-Ti-ZrB_2 composites after subjection to uniaxial compression tests. It can be observed that the main crack in Nb-Ti-ZrB_2 composites extends at an angle along the compressive direction. Many secondary cracks cause the spallation of fragments. In general, the failure takes place in a pseudoplastic fracture model [49]. At the beginning of the loading process, the cracks in the Nb-Ti-ZrB_2 composites initiate at defects and extend with increasing compressive stress. The increasing stress will generate a shear band [50] in the ductile (Ti,Nb,Zr)ss matrix and the cracks will extend along the shear band. Finally, the failure occurs in the Nb-Ti-ZrB_2 composites together with the existence of some secondary cracks [49].

(a)   (b)   (c)
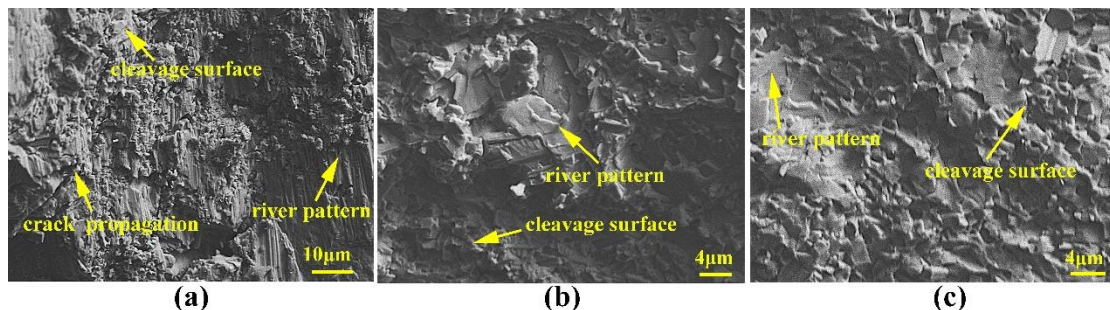
Fig. 9. Fracture surface for (a)Z1, (b)Z2, (c)Z3 after compression test.
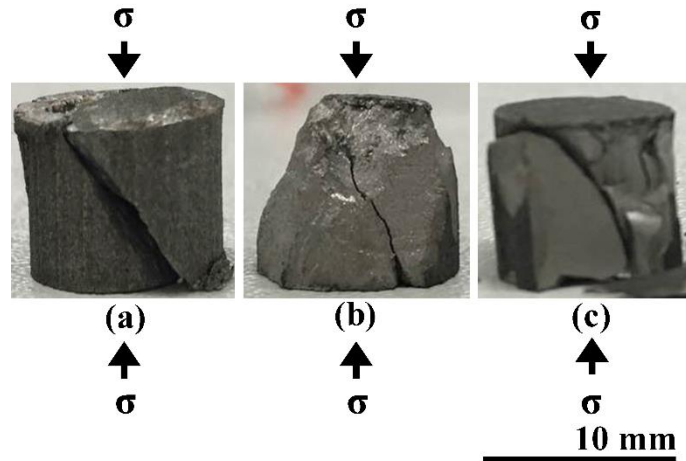
Fig. 10. Failure morphoologies for (a)Z1, (b)Z2, (c)Z3 after compression test.

5. Conclusion

Nb-Ti-ZrB$_2$ metal matrix ceramic composites with ZrB$_2$ content ranging from 0, 11vol.%, 23vol.% to 36vol.% were successfully hot pressed at 1600°C. The phase, microstructure, mechanical properties and failure processes were investigated. The main conclusions are summarized as follows:

(1) All the Nb-Ti-ZrB$_2$ composites consist of (Ti,Nb,Zr)ss, Ti-rich (Nb,Ti)B and Nb-rich (Ti,Nb)B phases. The decomposition of ZrB$_2$ is incomplete when the ZrB$_2$ content exceeds 36vol.% as there are large residual ZrB$_2$ particles displayed in the Nb-Ti-36vol.%ZrB$_2$ composite. The content of niobium and titanium borides increases with increasing ZrB$_2$ content. The needle-shaped Nb-rich (Ti,Nb)B and the nearly spherical Ti-rich (Nb,Ti)B display in the (Ti,Nb,Zr)ss solid solution matrix.

(2) Three different fracture modes are observed in the Nb-Ti-ZrB$_2$ composites: quasi-cleavage of the (Ti,Nb,Zr)ss, cleavage of the (Nb,Ti)B and pull-out of the (Ti,Nb)B. The addition of ZrB$_2$ particles to Nb-Ti alloys causes a decrease in fracture toughness due to ZrB$_2$ brittle fracture. The (Ti,Nb)B phase can weaken the damage to fracture toughness caused by ZrB$_2$ particles due

to crack bridging, crack defection and pull-out toughening mechanisms.

(3) The strength of the Nb-Ti-ZrB$_2$ composites depends on the combination influence of the strengthening mechanism caused by stiff (Nb,Ti)B and the weakening mechanism caused by (Ti, Nb)B and ZrB$_2$. The (Nb,Ti)B phase acts as an obstacle to hinder the dislocation motion in the matrix and then enhances the strength of Nb-Ti-ZrB$_2$ composites. However, the stress concentration around the needle-shaped (Ti, Nb)B phase and large residual ZrB$_2$ particles readily leads to crack initiation and accelerates the crack propagation with less compatible deformation, resulting in decreased strength. As a result, the strength of Nb-Ti-ZrB$_2$ composites decreases with increasing ZrB$_2$ content.

Acknowledgements

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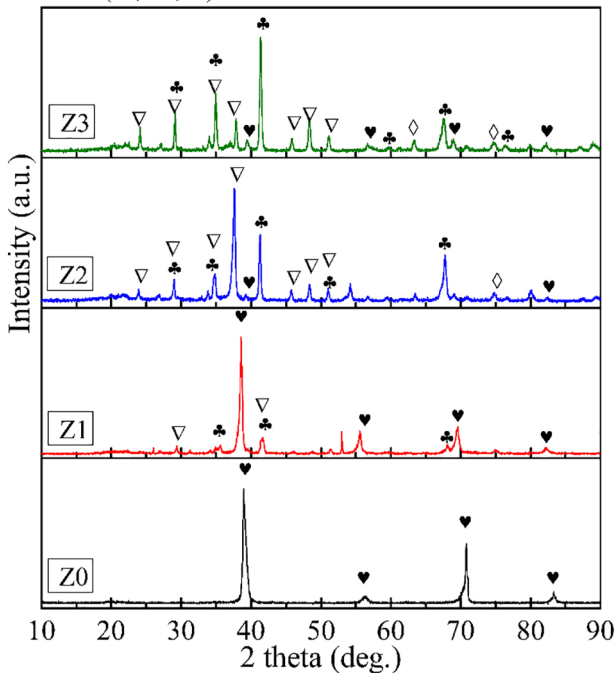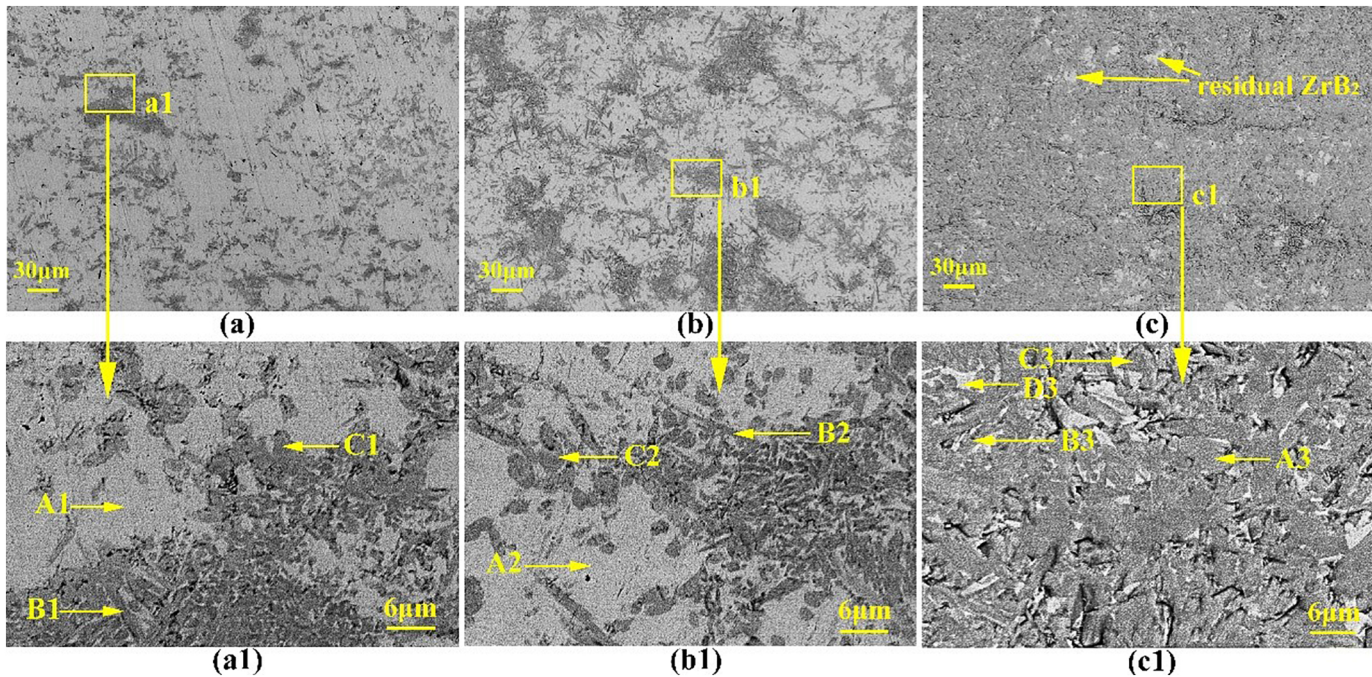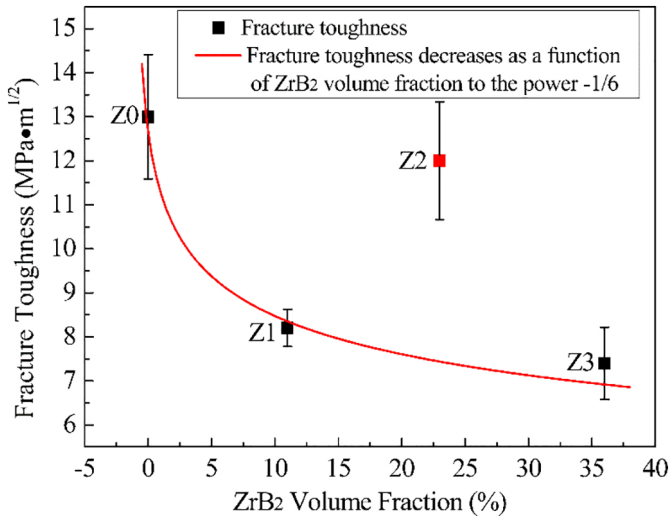
Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

crack deflection

crack branching

crack bridging

pull out

□ (Ti,Nb,Zr)ss ▬ (Ti,Nb)B ➜ crack direction

Figure 8

Figure 9

Figure 10