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Letter

Improving the strength of brazed joints with in situ synthesized TiB whiskers

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ABSTRACT

TiB whiskers have been in situ synthesized as reinforcements in 73Cu–27Ti (wt.%) active brazing filler alloy used for the joining of Al_2O_3 and Ti–6Al–4V alloy. The results show that TiB whiskers served as an effective reinforcement phase aid to decrease the residual stress and increase the shear strength of joints. The shear strength of the joint, containing 30 vol.% TiB whiskers was about 239% higher than that of the joint brazed without TiB whiskers.

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1. Introduction

Most of ceramics show brittleness and poor machinability, which makes it difficult to fabricate components of complex-shape and large-size. Joining of ceramic/metal or ceramic/ceramic can greatly overcome these weaknesses [1]. Active brazing is one of good joining methods. However, the quality of brazed joint is degraded by residual stress due to coefficient of thermal expansion (CTE) mismatch between metals and ceramics, and between brazing alloys and ceramics [2]. To solve this problem, low CTE materials (SiC [3–5], Al_2O_3 [6], TiC [3,7,8]) have been added into brazing filler alloy. However, direct addition method has many intrinsic limitations. The reinforcements are difficult to be distributed evenly in brazing alloy, reinforcements always have bad wetting ability with intermetallics, and reinforcement/brazing alloy interfaces are hard to control [9]. In situ synthesized reinforcements have considerable advantages of fine size, uniform distribution, relatively stable and impurity-free interfaces with matrix [10,11]. Although, Liu et al. improved the shear strength of the Si_3N_4 brazed joint remarkably by forming Ni–Ti intermetallics during brazing [12], little work is reported on in situ synthesizing TiB-whisker-reinforced active brazing alloy.

Cu–Ti + TiB_2 composite fillers were used to join Al_2O_3 and Ti–6Al–4V alloy in this paper. TiB whiskers were in situ synthesized in brazed joints during brazing. The typical microstructures of the brazed joints were analyzed. The role of TiB whiskers was discussed and the effects of the TiB whiskers content on microstructure and shear strength of the joints were also investigated.

2. Experimental

Al_2O_3 was sawn by diamond discs into specimens with size of 5.0 mm × 5.0 mm × 3.0 mm for microstructure examination and 4.0 mm × 4.0 mm × 3.0 mm for shear test. Ti–6Al–4V (TC4) alloy was cut into the specimens with size of 10.0 mm × 8.0 mm × 1.2 mm by wire electro-discharge machining. The surfaces to be brazed were grounded by 800 grit SiC paper and then all specimens ultrasonically were cleaned in acetone for 30 min.

The different content of TiB_2 powders (∼5 μm in diameter) was added to 73Cu–27Ti (wt.%) brazing filler metals, and then composite fillers were fabricated at room temperature under argon atmosphere by mechanical ball milling. The ball to powder weight ratio was 15:1, the rotation speed of value was 300 rpm and the milling time was 200 min. Fig. 1 shows the microstructure of the 65.9Cu–24.4Ti + 9.7TiB_2 (wt.%) as-milled powders as well as TiB_2 powders (marked by white circle) distributed uniformly in brazing filler alloy. Then the composite filler was mixed with binder into paste. The mixed paste was applied between Al_2O_3 and Ti–6Al–4V alloy by coating on the surface of Ti–6Al–4V alloy (∼100–200 μm). After that the assembly was brazed at 930 °C for 10 min in a vacuum furnace with the vacuum of 3.0×10^{-4} Pa. During brazing, the assembly was first heated to 450 °C at a rate of 20 °C/min, and held for 10 min to volatilize the binder and ensure that the brazing surfaces were clean. Then the temperature was continuously increased to 930 °C at a rate of 10 °C/min and held for 10 min. At last, the assembly was cooled down to 400 °C at 5 °C/min and then cooled in the furnace without power.

The microstructure of joints was analyzed by S-3400 scanning electron microscope (SEM) equipped with energy dispersive spectrometer (EDS). The shear strength of joints at room temperature was examined using Instron-1186 universal testing machine with a displacement rate of 0.5 mm/min. At least five specimens were tested for each experimental condition. After shearing, the joints fracture surfaces were also observed by SEM and EDS.

3. Results and discussion

Fig. 2 shows the microstructure of the joint brazed with 65.9Cu–24.4Ti + 9.7TiB_2 (wt.%) composite filler (synthesized

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Table 1
EDS compositional analysis result of the joints (T = 930 °C, t = 10 min).

Element (at.%)	O	Al	Ti	Cu	B	Possible phase
A	15.99	8.68	55.40	19.93	–	$Ti_4(Cu,Al)_2O$
B1	–	12.62	64.55	22.83	–	$Ti_2(Cu,Al)$
B2	–	21.80	66.23	11.97	–	$Ti_2(Cu,Al)$
C1	–	7.14	60.72	32.14	–	Ti_2Cu
C2	–	8.91	59.01	32.08	–	$(Ti,Al)_2Cu$
D	–	24.63	70.06	5.31	–	Ti_3Al
E	–	22.65	24.48	52.87	–	$AlCu_2Ti$
F	–	3.79	43.56	10.82	41.82	TiB

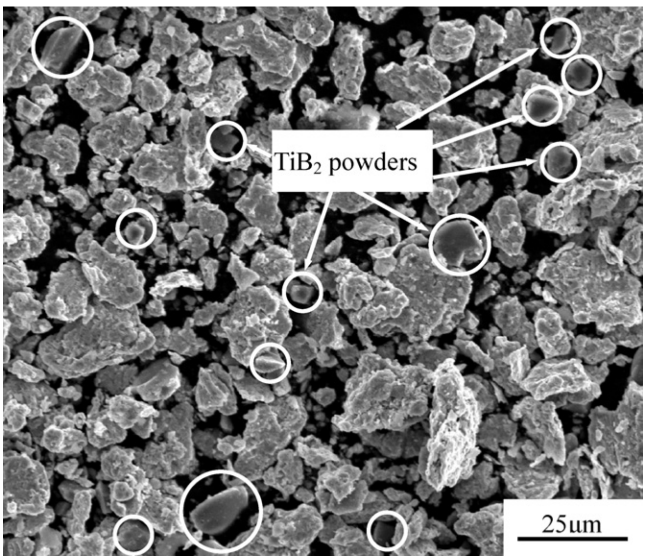

Fig. 1. SEM images of the 65.9Cu–24.4Ti + 9.7TiB_2 (wt.%) as-milled powders.

30 vol.% TiB whiskers) at 930 °C for 10 min. It is clear that there have no crack or void in the brazing layer. The joint can be divided into five layers which are marked with I, II, III, IV and V, respectively. The thickness of reaction layer I (phase A) adjacent to Al_2O_3 is about 2–3 μm. Layer II consists of dark gray phase B1, light gray phase C1 and dark phase D. Layer III contains a large number of dark gray phases B2. There are gray phase C2, light gray phase E, and needle-like black phase F contained in layer IV. The hypereutectoid organization Ti + Ti_2Cu constitutes a continuous reaction layer denoted layer V next to Ti–6Al–4V alloy, with a thickness of about 50 μm.

The compositions of A–E phases are measured by EDS, as listed in Table 1. Phase A can be determined to be $Ti_4(Cu,Al)_2O$. Phase B1, phase C1 and phase D in layer II proved to be $Ti_2(Cu,Al)$, Ti_2Cu and Ti_3Al, respectively. Phase B2 in layer III is $Ti_2(Cu,Al)$. Phase C2, E and F in layer IV indicate to be $(Ti,Al)_2Cu$, $AlCu_2Ti$ and TiB.

Fig. 3(a)–(f) shows microstructure of Al_2O_3/Ti–6Al–4V alloy joints brazed at 930 °C for 10 min. For brazed joints with TiB whiskers content less than 10 vol.%, significant cracking occurs next to Al_2O_3 (Fig. 3(a) and (b)). While no cracking is observed for brazed joints with 20–40 vol.% TiB whiskers (Fig. 3(c)–(e)). Serious cracks occur adjacent to Al_2O_3, when TiB content is 50 vol.%. In a word, most of cracks mainly occur nearby Al_2O_3, partially propagate into Al_2O_3, due to the residual stress between brazing layer and Al_2O_3.

Fig. 3(g)–(k) shows the morphology of TiB in layer IV. It can be seen that TiB whiskers have a good bonding with $(Ti,Al)_2Cu$ and $AlCu_2Ti$, without any obvious interfacial reaction or amorphous layer. Needle-like TiB whiskers are isolated and randomly oriented at low TiB volume fraction. Colonies of fine and well packed TiB whiskers appear at intermediate-to-high volume fraction. Elongate and coarse TiB whiskers form at the highest volume fraction. It is quite similar to what was reported by Sahay et al. in Ti–TiB composite [13]. There is no TiB_2 particle in joints, because Ti atoms dissolve continuously into brazing alloy from Ti–6Al–4V alloy. The Gibbs energy for TiB formation ($Ti + TiB_2 \rightarrow TiB$) at 930 °C is −8 kJ [14], proving formation of TiB is thermodynamically possible.

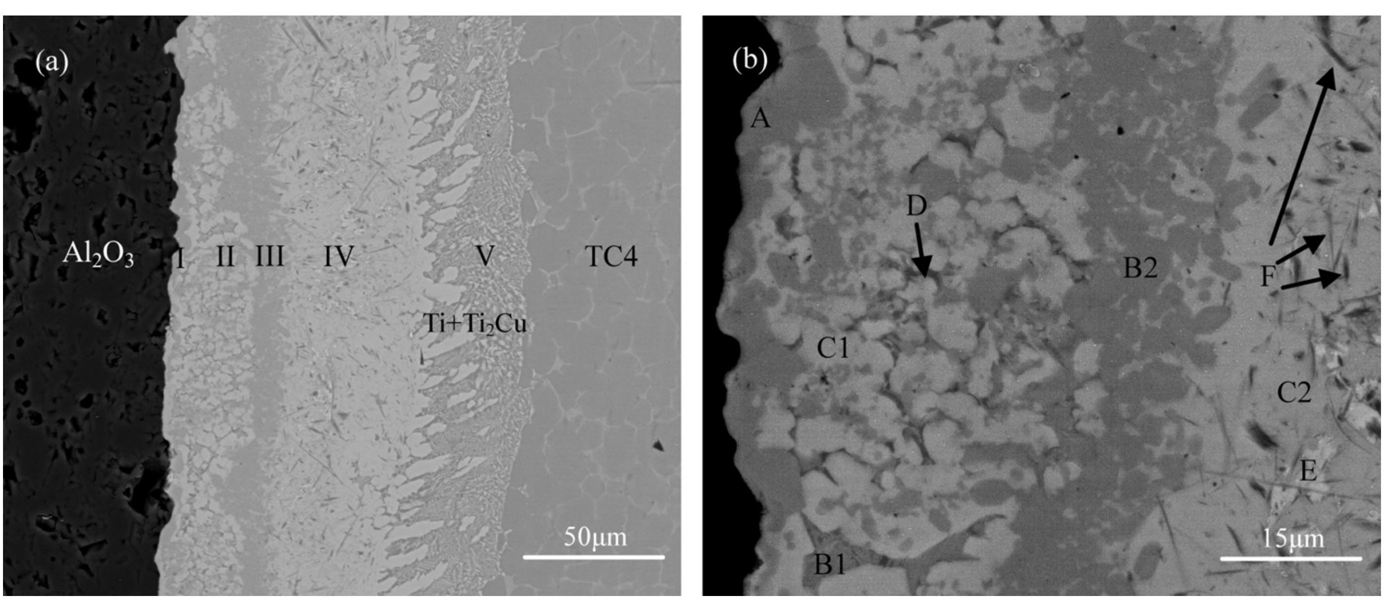

Fig. 2. SEM images of the Al_2O_3/Cu–Ti + TiB_2/Ti–6Al–4V alloy joint brazed at 930 °C for 10 min: (a) the whole joint; (b) the interface at Al_2O_3 side.

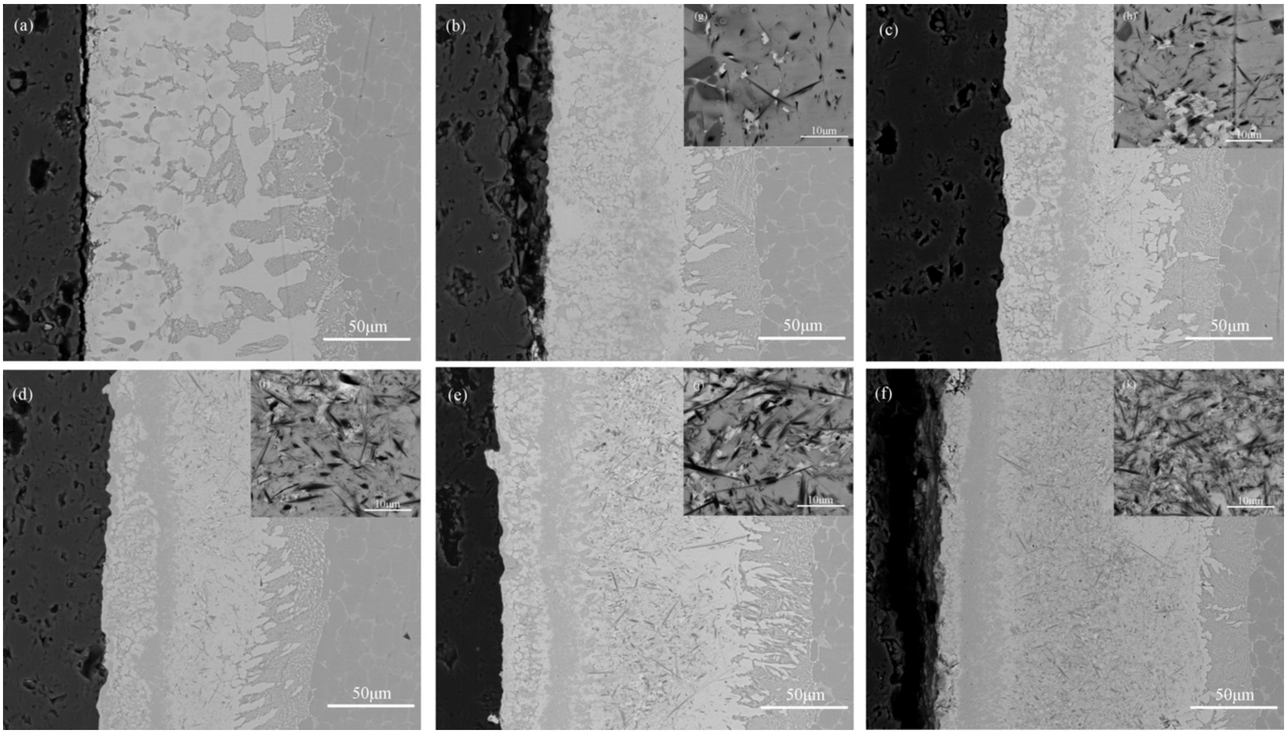

Fig. 3. SEM image of the Al_2O_3/Ti–6Al–4V alloy joints brazed with (a) Cu–Ti, (b) Cu–Ti + TiB_2 (10 vol.%TiB), (c) Cu–Ti + TiB_2 (20 vol.%TiB), (d) Cu–Ti + TiB_2 (30 vol.%TiB), (e) Cu–Ti + TiB_2 (40 vol.%TiB), (f) Cu–Ti + TiB_2 (50 vol.%TiB) at 930 °C for 10 min. (g)–(k) magnifications of layer IV in (b)–(f) respectively.

Fig. 4 shows the shear strength of Al_2O_3/Ti–6Al–4V alloy joints containing different volume fraction of TiB whiskers at 930° for 10 min. As can be seen, the shear strength increases from 42.25 to 143.30 MPa with TiB whiskers content ranging from 0 to 30 vol.%. The maximum shear strength of joint is about 239% higher than that of joints without TiB whiskers. Sufficient TiB whiskers content can match the CTE of brazing alloy to that of Al_2O_3, and then alleviate the joint residual stress. In situ synthesized TiB whiskers can also act as nucleation site for $(Ti,Al)_2Cu$ and $AlCu_2Ti$ grains refinement [15,16]. Furthermore, brazed joints are reinforced when TiB whisker reaches the critical size [17].

The shear strength of joints drops from 143.30 to 41 MPa when TiB whiskers content increases from 30 to 50 vol.%. It is believed that more TiB whiskers bring more reinforcement on the joint and

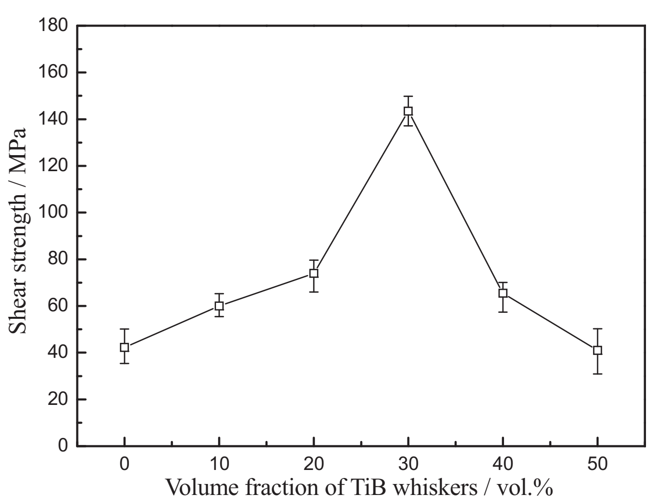

Fig. 4. Variation of shear strength of the Al_2O_3/Ti–6Al–4V alloy joints as a function of TiB whiskers content.

lead to a brazing layer with a higher elastic modulus [18]. Then the thermal stress occurred during brazing process cannot be relaxed effectively and a high thermal residual stress will be kept in the joint. Therefore, only suitable TiB whiskers content can joints shear strength be improved, although TiB whiskers can alleviate joints residual stress, refine $(Ti,Al)_2Cu$ and $AlCu_2Ti$ grains and act as reinforcements.

According to fracture of joints, all joints fail along Al_2O_3/brazing alloy interface, except the joint containing 30 vol.% TiB whiskers. Thus the brazed joints with Cu–Ti and Cu–Ti + TiB_2 (in situ synthesized 30 vol.% TiB) composite filler are selected as representatives to analyze. Joints fracture surfaces obtained by shear strength testing are shown in Fig. 5. The expansion path of cracks is shown in Fig. 5(a), exemplifying the residual stress exists in the interface between brazing layer and Al_2O_3. Compared with Fig. 3(a), (b), and (f), the fracture originates from the cracks at Al_2O_3/brazing alloy interface or within Al_2O_3.

Fig. 5(b) displays partly cup-cone marking dimples, those are indicative of ductile fracture. Based on the EDS results, failure occurs through the layer II, III, and IV of the joint rather than at Al_2O_3/brazing alloy interface or within Al_2O_3. It suggests that residual stress between brazing layer and Al_2O_3 is decreased. In Fig. 5(c), there are a large number of rupture TiB whiskers and pullout TiB whiskers on the fracture surface, indicating the presence of ideal TiB whiskers/$(Ti,Al)_2Cu$ or TiB whiskers/$AlCu_2Ti$ interfacial structure suitable for crack deflection, TiB whiskers pullout and rupture undoubtedly result in the increase in fracture toughness. Since the elastic modulus of TiB whiskers (~550 GPa) is much higher than that of $(Ti,Al)_2Cu$ (~150 GPa) or $AlCu_2Ti$ (~142 GPa), the modulus-load-transfer also increases toughness by transferring stress at a crack tip to regions remote from the crack tip, hence decreasing the stress intensity at the crack tip, further improving the joint strength [19]. In Fig. 5(d), cracks also appear in fracture surface, but they terminate expanding to the zone distributing TiB whiskers. That shows TiB whiskers make crack propagation more difficult. Therefore, the homogeneous distribution of TiB whiskers in $(Ti,Al)_2Cu$

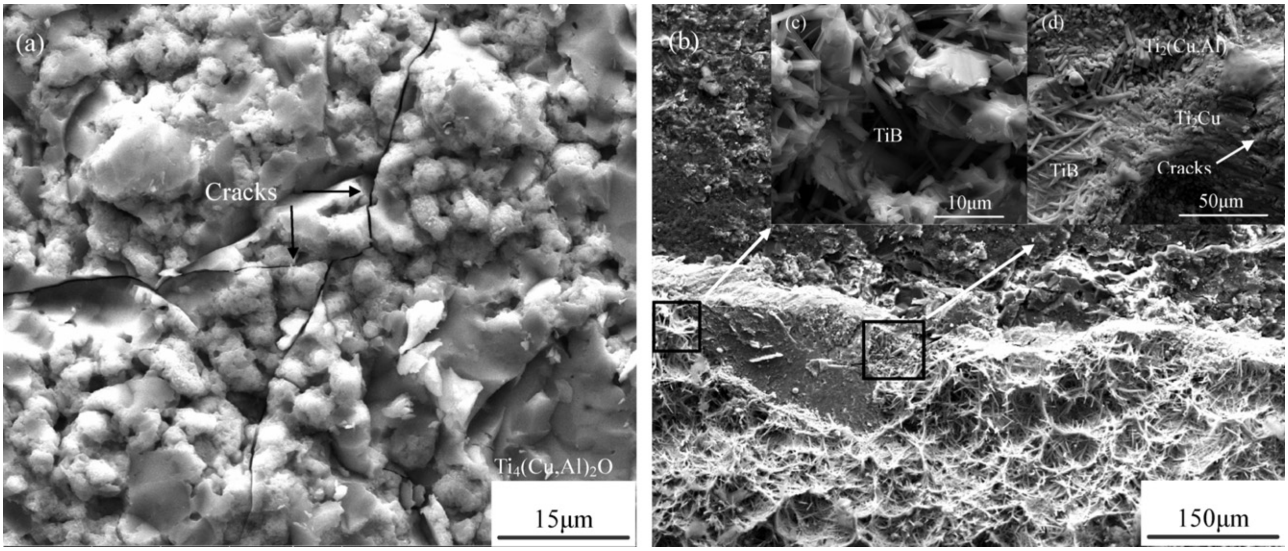

Fig. 5. SEM morphology of the fractural surfaces of Al_2O_3/Ti–6Al–4V alloy joints brazed with (a) Cu–Ti and (b) Cu–Ti + TiB_2 (30 vol.%TiB). (c) and (d) magnifications of the marked area in (b).

and $AlCu_2Ti$, and the suitable interfacial bonding of TiB/$(Ti,Al)_2Cu$ or TiB/$AlCu_2Ti$ may be the most important factors in effectively achieving the alleviation of residual stress, diffuse aggrandizement, and pinning aggrandizement of Al_2O_3/Ti–6Al–4V alloy joint.

4. Conclusions

(1) The typical microstructure of Al_2O_3/Cu–Ti + TiB_2/Ti–6Al–4V alloy joint brazed at 930 °C for 10 min is Al_2O_3/$Ti_4(Cu,Al)_2O$/Ti_2Cu + Ti_3Al + $Ti_2(Cu,Al)$/$Ti_2(Cu,Al)$/$(Ti,Al)_2Cu$ + $AlCu_2Ti$ + TiB/Ti_3Al + Ti_2Cu + (Ti + Ti_2Cu)/Ti–6Al–4V alloy.
(2) In situ synthesized TiB whiskers, as reinforcements, not only serve as an effective aid to alleviate the CTE mismatch between Al_2O_3 and brazing layer, but also decrease the detriment of great $(Ti,Al)_2Cu$ and $AlCu_2Ti$ by grain refinement.
(3) The maximum shear strength of the joints brazed with 65.9Cu–24.4Ti + 9.7TiB2 (wt.%) (in situ synthesized 30 vol.% TiB whiskers in joint) composite filler is 143.4 MPa, which is 239% higher than that of the joints brazed with Cu–Ti filler.
(4) Homogeneous distribution of TiB whiskers in $(Ti,Al)_2Cu$ and $AlCu_2Ti$ and intimate interfacial bonding of TiB/$(Ti,Al)_2Cu$ and TiB/$AlCu_2Ti$ make crack propagate more difficult.

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References

[1] G.W. Liu, W. Li, G.J. Qiao, H.J. Wang, J.F. Yang, T.J. Lu, J. Alloys Compd. 470 (2009) 163–167.
[2] H.H.K. Xu, J.B. Quinn, D.T. Smith, A.A. Giuseppetti, F.C. Eichmiller, Dent. Mater. 19 (2003) 359–367.
[3] J. Xiong, J. Huang, Z. Wang, G. Lin, H. Zhang, X. Zhao, Mater. Sci. Technol. 25 (2009) 1046–1050.
[4] M. Galli, J. Cugnoni, J. Botsis, J. Janczak-Rusch, Composites Part A 39 (2008) 972–978.
[5] G. Blugan, J. Kuebler, V. Bissig, J. Janczak-Rusch, Ceram. Int. 33 (2007) 1033–1039.
[6] J.G. Yang, H.Y. Fang, X. Wan, J. Mater. Sci. Technol. 21 (2005) 782–784.
[7] G.B. Lin, J.H. Huang, H. Zhang, X.K. Zhao, Mater. Trans. 47 (2006) 1261–1263.
[8] G.B. Lin, J.H. Huang, Powder Metall. 49 (2006) 345–348.
[9] B.S.S. Daniel, V.S.R. Murthy, G.S. Murty, J. Mater. Process. Technol. 68 (1997) 132–155.
[10] B. Reddy, K. Das, S. Das, J. Mater. Sci. 42 (2007) 9366–9378.
[11] C.X. Cui, Y.T. Shen, F.B. Meng, S.B. Kang, J. Mater. Sci. Technol. 16 (2000) 619–626.
[12] W. Liu, G. Elssner, M. Rühle, Mater. Sci. Eng. A 317 (2001) 153–162.
[13] S.S. Sahay, K.S. Ravichandran, R. Atri, B. Chen, J. Rubin, J. Mater. Res. 14 (1999) 4214–4223.
[14] Y.J. Liang, Y.C. Che, Handbook of Inorganic Thermodynamic Data, Northest University Press, Shenyang, 1996.
[15] R.K. Shiue, S.K. Wu, C.H. Chan, J. Alloys Compd. 372 (2004) 148–157.
[16] D. Hill, R. Banerjee, D. Huber, J. Tiley, H.L. Fraser, Scripta Mater. 52 (2005) 387–392.
[17] W. Baxter, Metall. Mater. Trans. A 23 (1992) 3045–3053.
[18] H. Xiong, C. Wan, Z. Zhou, J. Mater. Process. Technol. 75 (1998) 137–142.
[19] F. Ye, L.M. Liu, Y.J. Wang, Y. Zhou, B. Peng, Q.C. Meng, Scripta Mater. 55 (2006) 911–914.