

Interfacial microstructure and chemical stability during diffusion bonding of single crystal Al_2O_3 -fibres with Ni25.8Al9.6Ta8.3Cr matrix

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Abstract: BN coated Al_2O_3 fibre-reinforced NiAl-alloy composites were fabricated by hot pressing at 1 200–1 400 °C, and the interfacial microstructure and chemical stability of BN coated Al_2O_3 fibre-reinforced NiAl-alloy composites were investigated by scanning electron microscopy (SEM) and analytical transmission electron microscopy (TEM). It was found that the complicated chemical reactions and diffusion processes happened in the interface area between BN-layer and Ni25.8Al9.6Ta8.3 during the hot pressing at 1 200–1 400 °C. A continuous AlN-layer was formed at the interface due to the reaction between NiAl and BN. At the same time, Cr diffused extensively into the BN-layer and reacted with boron to form Cr boride precipitates (Cr_5B_3). In addition, a few particles of Ta-rich phase were also precipitated in NiAl matrix near the interface.

Key words: NiAl alloy composite; Al_2O_3 fibre; diffusion bonding

1 Introduction

NiAl alloys are attractive candidate materials to replace nickel-based superalloys because of their low density, large stoichiometric range, high melting point, good thermal conductivity, low raw materials cost and outstanding oxidation resistance[1–2]. However, NiAl alloy is brittle at low temperature and creeps rapidly at elevated temperatures[3–4]. Therefore, a new NiAl-base alloy (FG75) with about 9.6% Ta and 8.3% Cr (mass fraction) was developed, which exhibited higher strength at high temperatures with still tolerable brittleness at low temperature due to the formation of Laves phase and the precipitation of Cr[5]. Many studies were conducted on NiAl matrix composites reinforced with polycrystalline or single crystal continuous Al_2O_3 fibres[6]. The composites were fabricated by diffusion bonding, powder cloth process or similar powder metallurgy techniques.

It is well known that, the mechanical properties of composites are influenced by the bonding strength and microstructure of interface between strengthening phase and matrix. The previous work revealed that there is

excellent chemical compatibility between Al_2O_3 fibre and NiAl matrix with no chemical reaction during fabrication at high temperatures[7–8]. However, no improvement of high temperature performance was achieved for single crystal continuous Al_2O_3 fibre reinforced NiAl composites, both with strong or weak fibre/matrix interfacial bonding, due to the strength degradation of fibres[9].

Applying a coat on the fibre surface is an important way to control the structure and properties of the fibre/matrix interface. It was found that, by coating a thin BN layer on the Al_2O_3 fibre, the interfacial bonding strength between Al_2O_3 fibre and NiAl matrix can be improved, because a thin AlN layer can be formed at the NiAl/BN interface during the composite fabrication by diffusion bonding[10]. Hence, the characterization of interface structure and chemistry and their influence on the interface properties is vital for assessing the potential application of intermetallic matrix composites in practice. However, there is no any report on the interfacial microstructure and chemical stability between BN and FG75 matrix during diffusion bonding under high temperatures. Thus, in this work, FG75 matrix composites with the single crystal continuous Al_2O_3 fibre

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coated with BN are fabricated by diffusion bonding, and the interfacial reaction and microstructure are investigated.

2 Experimental

The matrix in the present study was an as-cast NiAl-Ta-Cr intermetallic compound with a nominal composition of Ni-25.8Al-9.6Ta-8.3Cr (mass fraction). The single crystal Al_2O_3 fibres with 125 μm in diameter and *c*-axis-oriented were used as reinforcement. The samples were cut from the ingot into the plates with the dimensions of 2.5 mm×6 mm×8 mm. The fibres were coated with 1 μm -thick BN layer by chemical vapour deposition (CVD) at about 1 000 °C. The fibres were sandwiched between two cleaned NiAl plates and mounted either onto a Shenck Umform-simulator equipped with a high temperature vacuum furnace for diffusion bonding in vacuum. Diffusion bonding was conducted under the conditions of temperature 1 200–1 400 °C and pressure 10–30 MPa in a vacuum of 5×10^{-3} Pa for 0.5–2 h.

The hot pressed samples were sliced perpendicularly to the fibre axis, and mechanically ground with a polishing machine. The interfacial microstructure was characterized using scanning electron microscopy (SEM) as well as analytical transmission electron microscopy (TEM).

3 Results

Figure 1 shows the SEM images of the interfaces between matrix and fibre in the samples fabricated at various temperatures. It can be seen that perfect contact between matrix and fibre was achieved after diffusion bonding in the temperature range of 1 200–1 400 °C for 2 h, but all of them exhibited a zone with chemical reaction products between BN and matrix during diffusion bonding. The reaction layer comprised two regions with various contrasts but no distinct interface. In the region near the matrix, continuous products with the grey contrast formed. Energy dispersive spectrometry (EDS) analysis, which is incapable of detecting light elements such as B and N, revealed that Al was the only element in the zone (Fig.2(a)). In the region close to the retained BN layer, a number of lighter particles precipitated. EDS analysis revealed that these particles primarily consisted of Cr (Fig.2(b)). The interfacial reaction layer was further developed with the temperature increasing. It should be noted that a few coarse phases formed in NiAl matrix near the BN/AlNi interface. EDS analysis revealed that these phases were always rich in Ta with some Cr (Fig.2(c)).

Figure 3(a) shows clearly a reaction layer with a

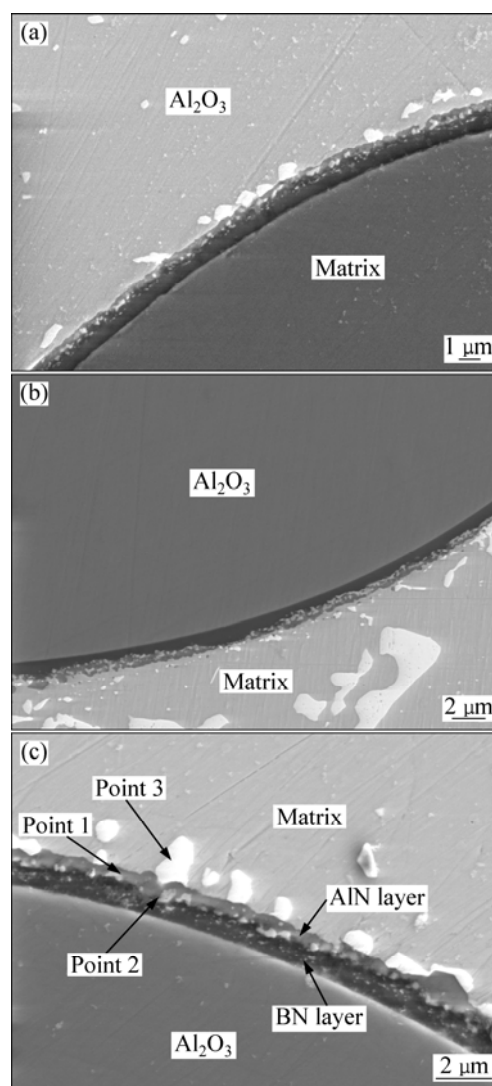


Fig.1 SEM images illustrating interfaces between Al_2O_3 fibre with BN coating and NiAl-Ta-Cr after diffusion bonding at different temperatures for 2 h: (a) 1 200 °C; (b) 1 300 °C; (c) 1 400 °C

thickness of about 0.6 μm at the NiAl/BN interface in the sample fabricated by diffusion bonding at 1 300 °C for 2 h. The corresponding element mappings are illustrated in Figs.3(b)–(f). It can be seen that, in the layer close to NiAl matrix, besides Al, it actually contained N, as seen in Fig.2(a). Along with the result in the previous study[11], these products could be determined to be AlN. While, the particles precipitated in the reaction layer primarily consisted of Cr, and some of them also contained B. Figure 4(a) shows a selected area electron diffraction (SAED) pattern obtained from a particle in the reaction layer. The diffraction pattern was found to be in good agreement with the $\langle 040 \rangle$ zone axis pattern of Cr_5B_3 , which has a tetragonal crystal structure with lattice parameters $a=0.546$ nm, $b=1.064$ nm. Thus, the particle could be determined to be Cr_5B_3 .

It should be noted that the coarse particles in the

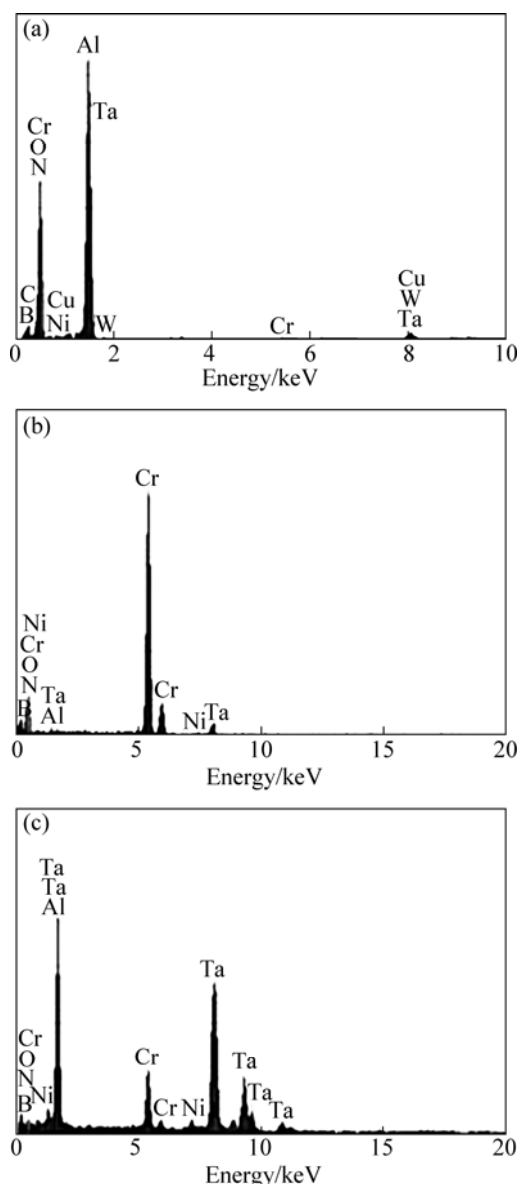


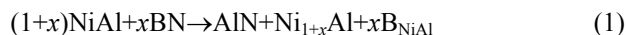
Fig.2 EDS spectra from different areas in Fig.1(c) at interface of NiAl/BN/Al₂O₃: (a) Point 1; (b) Point 2; (c) Point 3

NiAl matrix near the BN/NiAl interface primary consisted of Ta, but no B and N were detected by electron energy loss spectroscopy (EELS). SAED pattern recorded from the particle revealed that it has a tetragonal crystal structure, and the lattice parameters are in good agreement with that of β -Ta structure, as shown in Fig.4(b). Therefore, these particles could be determined to be Ta-rich phase.

4 Discussion

The interfacial microstructure and reaction of BN-coated single crystal Al₂O₃ fibre reinforced NiAl matrix composites were reported in Refs.[11–12]. A previous study reported that, during fabrication of the

composite by diffusion bonding at 1 400 °C for 2 h, a reaction between NiAl and BN occurred, and a layer of AlN with a thickness of about 100 nm formed at the NiAl/BN interface. On the basis of the reaction product, the reaction



was proposed to occur between NiAl matrix and BN coating, in which B_{NiAl} denotes B existing in the NiAl matrix. In the present study, NiAl-9.6Ta-8.3Cr was observed to react with BN in the temperature range of 1 200–1 400 °C, and the reaction products were more complicated. Besides AlN, a few Cr-rich or Cr boride particles were also found in the reaction layer. Similar to the reaction between BN and binary NiAl, an AlN layer formed at the interface of NiAl/BN near the NiAl matrix, and the AlN grains nucleated at the NiAl/BN interface and grew into the BN layer, which indicates that the reaction (1) has also occurred in the NiAl-9.6Ta-8.3Cr matrix composite. The reaction could occur at 1 200 °C, and is more extensive in comparison with that between BN and binary NiAl at the same fabrication conditions. This may be attributed to the composition of NiAl matrix, since the chemical activities of the constituents in a binary alloy system depend on the composition. The compositions of NiAl matrix after fabrication at 1 300 °C for 2 h were quantitatively measured by EDS. The statistical data revealed that the compositions of NiAl matrix are about 66% Ni, 30% Al, 1% Ta and 3% Cr (mass fraction). The solution of ~4% (Ta+Cr) in NiAl matrix may increase the chemical activity of Al in NiAl.

The formation of AlN at the interface of BN/NiAl may produce free Ni and B atoms. According to the binary Al-Ni phase diagram[13], NiAl can exist over an extended compositional range. EDS analysis also revealed that no Ni was detected in the reaction layer and BN, and no significant difference between the Ni concentration at the interface in NiAl and that away from the interface in NiAl, which indicates a diffusion flow of Ni atoms from interface into NiAl matrix. The question is where the free B atoms produced in the reaction between BN and NiAl are. Since the boron solubility is very low in metals and alloys[14], no measurable B content was detected outside the BN by EELS in both the previous and the present studies. Thus, it was speculated that the B atoms liberated through the interface reaction probably had segregated to the grain boundaries of NiAl[6]. However, for the FG75 alloy, the grain boundaries were occupied by Laves phase formed during casting. Therefore, we speculate that the free B atoms may diffuse into the retained BN layer or segregate to the AlN/BN interface and the grain boundaries of AlN.

From a pseudo-binary NiAl-Cr phase diagram[15], the solid solubility of Cr in NiAl is estimated to be 3%,

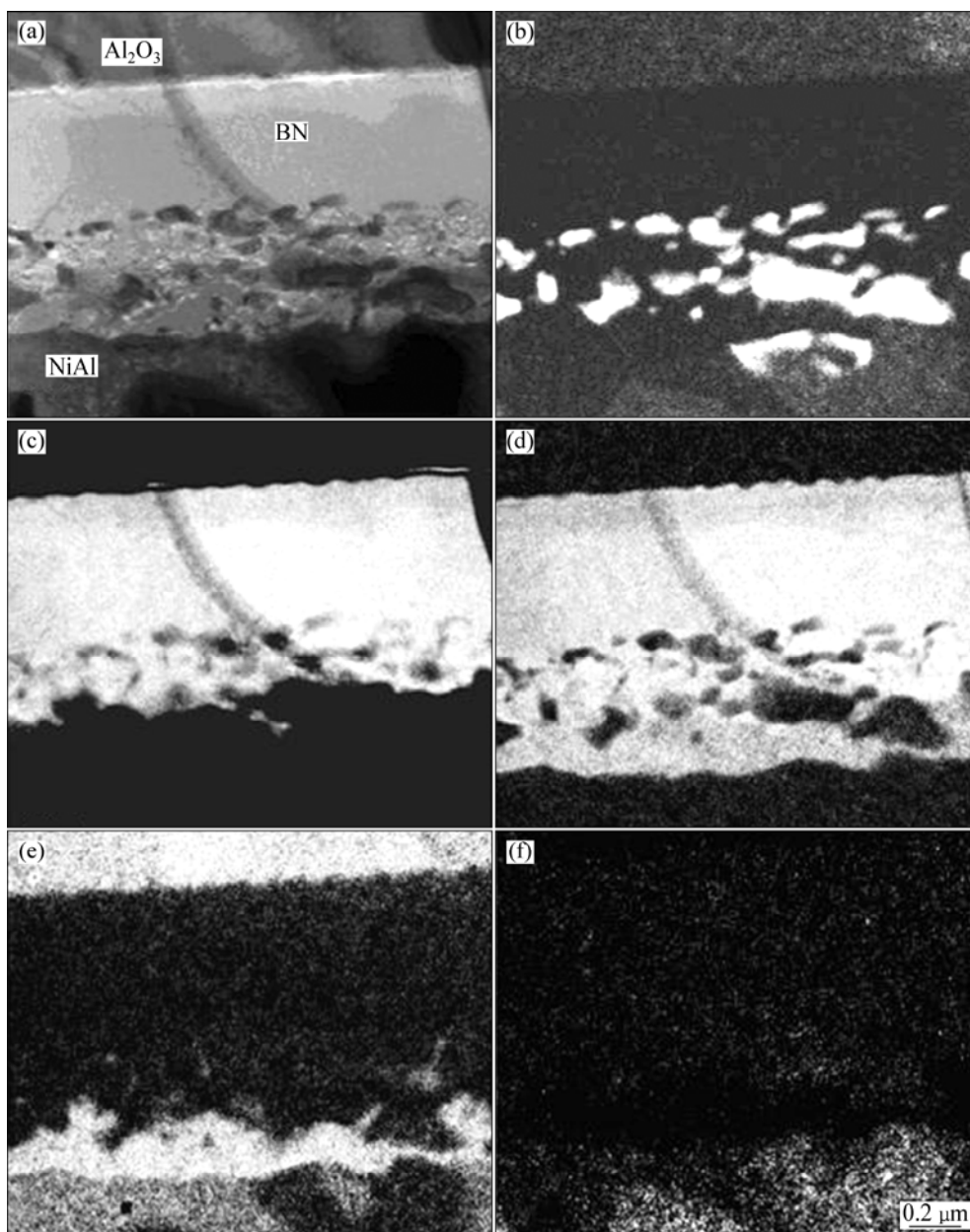


Fig.3 TEM image (a) at interface of BN/NiAl in diffusion bonded sample at 1 300 °C for 2 h and corresponding element mappings of Cr (b), B (c), N (d), Al (e) and Ta (f)

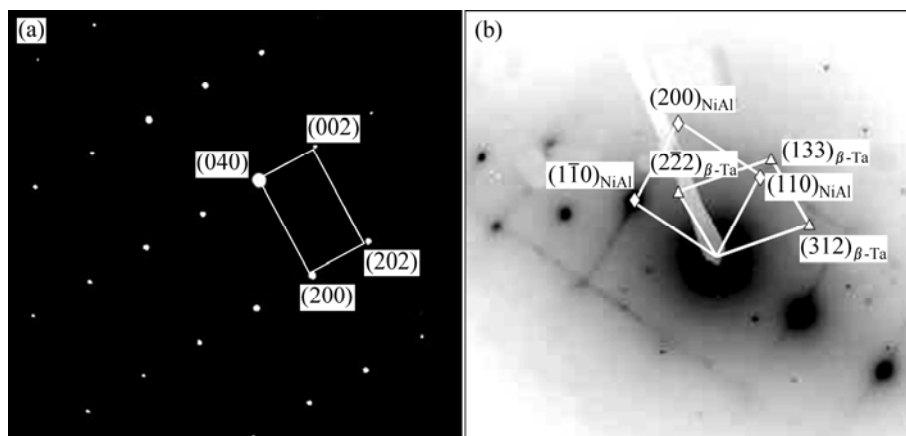


Fig.4 SAED patterns of particles in reaction layer: (a) Cr_5B_3 particles; (b) β -Ta

5.8% and 6.4% (mass fraction) at 25, 1 000, and 1 050 °C, respectively. Higher Cr content induces Cr precipitation in the NiAl matrix. Thus, a few spherical Cr-rich phases could be observed in the as-cast FG75 alloy. It should be noted that, during the fabrication of the composite in the temperature range of 1 200–1 400 °C, a few Cr-rich particles and Cr borides could be observed in the reaction layer. It is indicated that a diffusion flow of Cr atoms from NiAl matrix to BN layer occurred, and some Cr atoms reacted with B to form Cr borides. The reasons of the extensive diffusion of Cr atoms into BN layer are unclear yet. According to B-Cr diagram[16], a series of Cr borides with high thermal stability can be formed. The reaction between Cr and B atoms may drive the Cr atoms to diffuse from NiAl into BN layer.

It was found that, during heating at 1 200 and 1 400 °C, a number of fine particles had precipitated in the NiAl matrix. These particles were determined to be TaCr₂ Laves phase with the cubic structure (C15). The precipitation of the Laves phase may be attributed to the supersaturation of Ta in the as-cast NiAl matrix. The interface of BN/NiAl can provide good positions for the nucleation of the Laves phase due to the higher diffusion coefficient of Ta and lower nucleation energy. So, it can be found that a few coarse particles formed at the interface of BN/NiAl during fabrication of the composition in the temperature range of 1 200–1 400 °C. However, it should be noted that the microanalysis revealed that these particles are rich in Ta and have Ta structure. As mentioned above, the Cr diffused extensively into the BN-layer and reacted with B atoms to form Cr boride precipitates, which may consume the Cr atoms in the Laves phases near the interface, resulting in the formation of the Ta-rich particles near the interface.

5 Conclusions

1) BN coated Al₂O₃ fibre-reinforced NiAl-alloy composites were fabricated by hot pressing at 1 200–1 400 °C. The complicated chemical reactions and diffusion processes took place in the interface area between BN-layer and NiAl-2.5Ta-7.5Cr during the hot pressing at 1 200 °C–1 400 °C.

2) The reactions between BN and NiAl-2.5Ta-7.5Cr were more extensive in comparison with that between BN and binary NiAl at the same fabrication conditions. Besides a continuous AlN-layer formed at the interface between NiAl and BN, Cr diffused extensively into the BN-layer and reacted with boron to form Cr boride precipitates (Cr₃B₃). In addition, a few particles of

Ta-rich phase also precipitated in NiAl matrix near the interface.

References

- [1] MIRACLE D B. The physical and mechanical properties of NiAl [J]. *Acta Metallurgica et Materialia*, 1993, 41(3): 649–684.
- [2] TANG L Z, ZHANG Z G, LI S S, GONG S K. Mechanical behaviors of NiAl-Cr(Mo)-based near eutectic alloy with Ti, Hf, Nb and W additions [J]. *Transactions of Nonferrous Metals Society of China*, 2010, 20(2): 212–216.
- [3] ZHANG Guang-ye, GUO Jian-ting, ZHANG Hu. High-temperature creep behavior of NiAl-25%Cr alloy [J]. *The Chinese Journal of Nonferrous Metals*, 2006, 16(11): 1882–1887. (in Chinese)
- [4] SHENG L Y, ZHANG W, GUO J T, ZHOU L Z, YE H Q. Microstructure evolution and mechanical properties' improvement of NiAl-Cr(Mo)-Hf eutectic alloy during suction casting and subsequent HIP treatment [J]. *Intermetallics*, 2009, 17(12): 1115–1119.
- [5] ZEUMER B, SAUTHOFF G. Deformation behaviour of intermetallic NiAl-Ta alloys with strengthening Laves phase for high-temperature applications III. Effects of alloying with Cr [J]. *Intermetallics*, 1998, 6(5): 451–460.
- [6] MICHALSKI A, JAROSZEWICZ J, ROSIŃSKI M, SIEMIASZKO D. NiAl-Al₂O₃ composites produced by pulse plasma sintering with the participation of the SHS reaction [J]. *Intermetallics*, 2006, 14(6): 603–606.
- [7] GUO Jian-ting, XIE Yi. Review on continuous fiber-reinforced NiAl matrix composites [J]. *Chinese Journal of Materials Research*, 2007, 21(2): 113–118. (in Chinese)
- [8] HU W, WEIRICH T, HALLSTEDT B, CHEN H, ZHONG Y, GOTTSTEIN G. Interface structure, chemistry and properties of NiAl composites fabricated from matrix-coated single-crystalline Al₂O₃ fibres (sapphire) with and without an hBN interlayer [J]. *Acta Materialia*, 2006, 54(9): 2473–2488.
- [9] ZHONG Y, HU W, ELDRIDGE J I, CHEN H, SONG J, GOTTSTEIN G. Fiber push-out tests on Al₂O₃ fiber-reinforced NiAl-composites with and without hBN-interlayer at room and elevated temperatures [J]. *Materials Science and Engineering A*, 2008, 488(1–2): 372–380.
- [10] BOWMAN R R, MISRA A K, ARNOLD S M. Processing and mechanical-properties of Al₂O₃ fiber-reinforced NiAl composites [J]. *Metallurgical and Materials Transactions A*, 1995, 26(3): 615–628.
- [11] WEN K Y, HU W P, REICHERT K, GOTTSTEIN G. Interfacial microstructure and reaction of BN-coated single crystal Al₂O₃ fiber reinforced NiAl matrix composites [J]. *Journal Materials Science*, 2002, 37(6): 1253–1258.
- [12] WEN K Y, REICHERT K, HU W P, GOTTSTEIN G. Interfacial thermal stability in BN-coated continuous Al₂O₃ fiber-reinforced NiAl composites [J]. *Materials Science and Engineering A*, 2004, 367(1–2): 33–39.
- [13] MASSALSKI T B, OKAMOTO H. Binary alloy phase diagrams [M]. Metals Park, OH: American Society for Metals, 1990: 183–184.
- [14] WANG L, ARSENAULT R J. Interfaces in XD processed TiB₂/NiAl composites [J]. *Metall Trans A*, 1991, 22(12): 3013–2018.
- [15] TIWARI R, TEWARI S N, ASTHANA R, GARG A. Development of NiAl-based intermetallic alloys—Effect of chromium addition [J]. *Materials Science and Engineering A*, 1995, 192: 356–363.
- [16] CAMPBELL C E, KATTNER U R. Assessment of the Cr-B system and extrapolation to the Ni-Al-Cr-B quaternary system [J]. *Calphad*, 2002, 26(3): 477–490.

扩散连接条件下 Al_2O_3 纤维与 $\text{Ni}_{25.8}\text{Al}_{19.6}\text{Ta}_{8.3}\text{Cr}$ 基体的界面结构及稳定性

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摘 要: 在 1 200–1 400 °C 下采用热压扩散的方法制备 BN 包覆 Al_2O_3 纤维增强 NiAl 基复合材料, 利用扫描电子显微镜(SEM)和透射电子显微镜(TEM)研究其界面的显微结构和化学热稳定性。结果表明, 在 BN 层与 $\text{Ni}_{25.8}\text{Al}_{19.6}\text{Ta}_{8.3}$ 的界面处发生了元素的扩散并伴随有复杂的化学反应发生。在 NiAl 和 BN 界面形成了连续的 AlN 层, Cr 原子扩散到 BN 层中与 B 发生反应生成 Cr_5B_3 , 还有少量的富 Ta 相在近 NiAl 侧界面处生成。

关键词: NiAl 基复合材料; Al_2O_3 纤维; 扩散连接

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