Effects of Forming Conditions and TiC–TiB₂ Contents on the Microstructures of Self-Propagating High-Temperature Synthesized NiAl–TiC–TiB₂ Composites

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Abstract The NiAl–TiC–TiB₂ composites were processed by self-propagating high-temperature synthesis (SHS) method using raw powders of Ni, Al, Ti, B₄C, TiC, and TiB₂, and their microstructure and micro-hardness were investigated. The TiC–TiB₂ in NiAl matrix, with contents from 10 to 30 wt%, emerged with the use of two methods: in situ formed and externally added. The results show that all final products are composed of three phases of NiAl, TiC, and TiB₂. The microstructures of NiAl–TiC–TiB₂ composites with in situ-formed TiC and TiB₂ are fine, and all the three phases are distributed uniformly. The grains of NiAl matrix in the composites have been greatly refined, and the micro-hardness of NiAl increases from 381 HV₁₀₀ to 779 HV₁₀₀. However, the microstructures of NiAl–TiC–TiB₂ composites with externally added TiC and TiB₂ are coarse and inhomogeneous, with severe agglomeration of TiC and TiB₂ particles. The samples containing externally added 30 wt% TiC–TiB₂ attain the micro-hardness of 485 HV₁₀₀. The microstructure evolution and fracture mode of the two kinds of NiAl–TiC–TiB₂ composites are different.

KEY WORDS: NiAl–TiC–TiB₂ composite; Self-propagating high-temperature synthesis (SHS);
Forming condition; TiC–TiB₂ content; Microstructure

1 Introduction

Ni–Al intermetallics have received noticeable attention as attractive structural materials for high temperature applications on account of its high melting point, low density, high specific strength and good oxidation, etc. [1–3]. However, the relatively poor low-temperature toughness and high-temperature strength limit their extensive applications [4, 5]. It has been reported that the properties of Ni–Al intermetallics can be dramatically improved by the in situ formed and externally added particulates including

TiC [6], TiB₂ [7], Al₂O₃ [8], ZrC [9], and NbB₂ [10] particles. The considerably improved mechanical properties [10–12] of the NiAl alloy are mainly due to the ceramic particulates which are isotropic and stable at high temperatures, acting as obstacles of the grain growth and dislocation glide in the slip planes [8, 10]. Sheng et al. [6] have measured the mechanical properties of NiAl–TiC–Al₂O₃ composite, and the results showed that the NiAl–TiC–Al₂O₃ composite possessed better mechanical properties especially at room temperature, and they ascribed to the fine microstructure and pre-deformation caused by hot extrusion. Xu et al. [12] have reported the significantly enhanced ultimate compressive yield strength and fracture toughness of the NiAl–Al₂O₃ composite fabricated by pulse current auxiliary sintering (PCAS). The main strengthening-toughening mechanisms are grain refinement strengthening and Al₂O₃ dispersion strengthening. Thus, NiAl matrix composites which are reinforced with ceramic particulates seem to have wide applications in which

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Fig. 1 SEM images showing the morphologies of raw materials of Ni **a**, Al **b**, Ti **c**, B₄C **d**, TiB₂ **e**, TiC **f**

corrosion and wear resistances are required, especially at high temperatures [13, 14]. Among these dispersoids, TiC–TiB₂ are particularly suitable in this respect due to their special properties including high melting point, low density, high hardness, high wear resistance, a good strength and toughness, and high thermal shock resistance [15, 16]. Some studies have showed that the addition of TiB₂ or TiC as a particulate reinforcement to NiAl could increase the hardness, flexural strength, and fracture toughness of the composites [13, 17]. However, there is a lack of study on

the NiAl matrix composites reinforced with the TiC–TiB₂ multiphase ceramics.

In recent years, NiAl matrix composites have been prepared by a variety of methods, including hot-pressing reaction sintering (HPRS) [18], exothermic dispersion (XD) [19], mechanical alloying (MA) [20], pressureless melt infiltration [21], self-propagating high-temperature synthesis (SHS) [22], etc. Among these techniques, SHS has the advantages of being a simple process, high efficiency, low cost, etc., and is an attractive method in the

preparation of ceramics, intermetallics and their composites [23].

In this work, the NiAl matrix composites reinforced with dual ceramic particulates of TiC and TiB₂ have been fabricated by the SHS reaction using Ni, Al, Ti, B₄C, TiC, and TiB₂ as raw materials. Ti and B₄C are selected, which react with each other during fabrication and produce in situ-formed TiC–TiB₂. The aim of the present investigation is to study the effects of the in situ-formed and externally added TiC–TiB₂ particulates on the microstructure and micro-hardness of NiAl compounds and to understand the different forming processes of microstructures in the two systems.

2 Experimental

NiAl–TiC–TiB₂ composites were fabricated by SHS process using raw pure powders of Ni (99.5% purity, 38–48 μm), Al (99% purity, 48–75 μm), Ti (99.5% purity, 38–48 μm), B₄C (94% purity, 7–10 μm), TiB₂ (98% purity, 2–10 μm), and TiC (99.5% purity, ~25 μm). Morphologies of all raw powders are presented in Fig. 1.

The TiC–TiB₂ dual-phase reinforcements were introduced into the NiAl matrix by two methods: (a) in situ formed through reaction between Ti and B₄C powders; (b) externally added of TiC and TiB₂ powders [24–25]. Two reactions occurred between raw powders of Ti, Al, B₄C are described as below, as well as their Gibbs free energies (ΔG^0 , in J/mol).

The molar proportions of Ni/Al, Ti/B₄C, and TiC/TiB₂ in powder blends were fixed to 1:1, 3:1, and 1:2, respectively, for both fabrication processes according to stoichiometry in reactions (1) and (2). The purpose is to compare the composites fabricated by different processes but having same composition. The detailed ingredients of starting materials prepared by methods A and B and their symbols are listed in Table 1. A simple NiAl intermetallic (symbol “O”) was also prepared for comparison with composites reinforced by TiC and TiB₂. The powder blends were dry mixed sufficiently by a multi-dimensional (3-D) blender for about 10 h to produce a homogeneous powder mixture. The blends were then uniaxially cold compacted into cylindrical pellets in a steel die of 20 mm in diameter at the pressure of 85 MPa. Each compacted pellet weighted approximately 15 g. The compacted pellets were then ignited by an electrifying tungsten wire. The compacted

Table 1 The molar proportions of starting materials and their symbols

Scheme	Sample	Number
Pure NiAl	Ni + Al	O
A	Ni + Al + 10 wt%(3Ti + B ₄ C)	A-10
	Ni + Al + 20 wt%(3Ti + B ₄ C)	A-20
	Ni + Al + 30 wt%(3Ti + B ₄ C)	A-30
B	Ni + Al + 10 wt%(TiC + 2TiB ₂)	B-10
	Ni + Al + 20 wt%(TiC + 2TiB ₂)	B-20
	Ni + Al + 30 wt%(TiC + 2TiB ₂)	B-30

Fig. 2 Schematic diagram of SHS reaction initiated by electrifying tungsten wire

pellets by methods A and B listed in Table 1 were pre-heated to 300 °C before igniting. The compacted and ignited pellets were then cooled down in the air. A schematic diagram of SHS reaction initiated by electrifying tungsten wire is shown in Fig. 2.

The phases in the ignited products were identified by X-ray diffraction (XRD, D/Max 2500PC Rigaku, Japan). The compositions were measured by electron probe microanalysis (EPMA, JXA-8230, Japan). The microstructures and fracture surfaces of the samples (O, A-20, B-20) were observed by scanning electron microscope (SEM, KYKY2800B). Vickers micro-hardness was measured using the FM-700 tester under the load of 1 N and dwell time of 10 s. Measurements were conducted on 5 points for each sample in order to achieve reliable average value of the hardness.

3 Results

3.1 Phase Analysis

Figure 3 shows the XRD patterns of the NiAl matrix composites with various contents of the ceramic particulates (TiC, TiB₂) ranging from 10 to 30 wt%, and

Fig. 3 X-ray diffraction spectra of products: **a** Ni + Al + $x(3\text{Ti} + \text{B}_4\text{C})$, **b** Ni + Al + $x(\text{TiC} + 2\text{TiB}_2)$

Fig. 4 SEM images showing the microstructures of in situ formed NiAl–TiC–TiB₂ composites with different contents of (3Ti + B₄C): **a** 0, **b** A-10, **c** A-20, **d** A-30

compared with the XRD pattern of pure NiAl intermetallic. It indicates that the synthetic methods of the ceramic particulates have no effect on the phase structure in the

composites. As can be seen in Fig. 3, the peaks corresponding to NiAl, TiB₂, and TiC are present in all samples, indicating that the reactions (1) and (2) accomplished

completely without any remaining of raw ingredients. Moreover, the intensity of the ceramic phases increases with increasing amount of $3\text{Ti} + \text{B}_4\text{C}$ or $\text{TiC} + 2\text{TiB}_2$, while the intensity of NiAl decreases relatively, as shown in Fig. 3.

3.2 Microstructure

The microstructures of the simple NiAl intermetallic (O) and in situ-formed NiAl–TiC–TiB₂ composites with different contents of $(3\text{Ti} + \text{B}_4\text{C})$ (A-10, A-20, A-30) are shown in Fig. 4. The grains of the simple NiAl intermetallic as well as some secondary phases appeared at the grain boundaries can be clearly observed, and the average grain size is about 40 μm , as can be seen in Fig. 4a. After adding $(3\text{Ti} + \text{B}_4\text{C})$ blend, there are some dark or gray fine particles formed and distributed along the NiAl grain boundaries, see Fig. 4b. With increasing $(3\text{Ti} + \text{B}_4\text{C})$ contents, the amount of fine particles in the composites increased apparently, see Fig. 4c and d. It can also be seen that the grain size of NiAl matrix decreased from 40 to 5 μm approximately, and comparing Fig. 4a with Fig. 4d, it indicates the refinement effect of adding $(3\text{Ti} + \text{B}_4\text{C})$ blend on the NiAl matrix. Furthermore, most of the fine particulates in A-10 and A-20 samples distribute discretely at the NiAl grain boundaries, as can be seen in Fig. 4b and

c. When the content of $3\text{Ti} + \text{B}_4\text{C}$ increases to 30 wt%, continuous distribution of the fine particulates along the NiAl grain boundaries, and some within the NiAl grains, was observed; see, Fig. 4d.

The close views at high magnification on the polished and fracture surfaces of A-30 sample are shown in Fig. 5a and b. The detailed morphologies of these fine particulates were revealed to be rectangle, hexagon or quasi-spherical shapes. The average sizes of these fine particulates are less than 2 μm . Further elemental analyses by EDS on particulates pointed by arrows in SEM images in Fig. 5 were conducted. It was found that the rectangle and hexagon particulates are TiB₂, while quasi-spherical particulates are TiC which agrees well with the results reported in the literatures [15, 25]. The EDS spectra of TiB₂ and TiC are presented in Fig. 5.

The microstructures of NiAl–TiC–TiB₂ composites fabricated by method B are shown in Fig. 6, which are noticeably different from the microstructures of composites processed by method A. Firstly, the segregation of the ceramic particulates along the NiAl grain boundary is more obvious. Secondly, the size of the ceramic particulates is not uniform, and the average particle size is much bigger than the size of in situ-formed TiC and TiB₂ particles. Similar to composites made by method A, the NiAl grain size also decreased evidently with the addition of

Fig. 5 Microstructure **a**, fracture graph **b**, observed by SEM, and EDS spectra detected on TiB₂ and TiC phases in the NiAl–TiC–TiB₂ composites with 30 wt% $(3\text{Ti} + \text{B}_4\text{C})$

Fig. 6 SEM images showing the microstructures of NiAl–TiC–TiB₂ composites with different contents of (TiC + 2TiB₂): **a** B-10, **b** B-20, **c** B-30

TiC + 2TiB₂ particulates, from 40 to 10 μm approximately, see in Figs. 4a and 6c.

3.3 Micro-hardness Measurement

The micro-hardness was tested on the NiAl matrix only for all samples. Figure 7 shows the average micro-hardness values of the composites fabricated by methods A and B. It can be seen that with increasing amount of in situ-formed reinforcing particulates (A samples), the micro-hardness of the NiAl matrix was improved significantly. Meanwhile, for the composites with externally added TiC + TiB₂ particles (B samples), the increase of micro-hardness is very limited. The highest hardness values of the composites fabricated by method A and method B are 779 HV₁₀₀ and 485 HV₁₀₀, respectively. Both are higher than micro-hardness of the simple NiAl (sample O), which is approximately 381 HV₁₀₀. The increase of the micro-hardness of NiAl matrix may be attributed to the grain refinement and residual stress generated during ignition due to the difference in the coefficients of thermal expansion between the matrix and ceramic particulates, resulting in the high density of dislocations [6, 26]. In addition, the average values of micro-hardness in Fig. 7 are very consistent with the results reported by Shokati and Zhu [11, 27].

The fracture surfaces of the simple NiAl intermetallic and composites of A-20 and B-20 are shown in Fig. 8. The fracture mode of the simple NiAl is mainly transgranular cleavage, see Fig. 8a. When the ceramic particulates were in situ formed in composite A-20, the fracture mode of the composite changes to a mode of combined intergranular and transgranular fracture, see Fig. 8b. However, when the ceramic particulates were externally added in B-20 composite, the fracture surface reveals intergranular fracture completely without any trace of transgranular feature. Generally, intergranular fracture consumes less energy than transgranular fracture during deformation or damage and results in the lower ultimate fracture strength of the composites.

Fig. 7 Average micro-hardness values measured on NiAl matrix of the NiAl–TiC–TiB₂ composites: **a** Ni + Al + $x(3\text{Ti} + \text{B}_4\text{C})$, **b** Ni + Al + $x(\text{TiC} + 2\text{TiB}_2)$

4 Discussion

The contents and synthetic method of TiC–TiB₂ have great effect on the microstructures and micro-hardness of NiAl–TiC–TiB₂ composites. For the samples fabricated by method A, in situ-formed TiC and TiB₂ distribute mainly along the NiAl grain boundaries, and form nearly a network with a relatively uniform distribution. This could separate the NiAl matrix to different parts as Fig. 4b–d, and impede the abnormal coarsening of NiAl grains in each part. This might decrease the harmful effect of coarsening grains on the mechanical properties of the composite. Comparatively, the inhomogeneous distribution and severe agglomeration of TiC and TiB₂ particles in the samples made by method B are detrimental to the mechanical properties of the composite.

During fabrication by method A, the decomposition-precipitation process is considered to be the dominant mechanism for the in situ-formed ceramic particulates as

Fig. 8 SEM fractographs of simple NiAl **a**, Ni + Al + 20%(3Ti + B₄C) **b**, Ni + Al + 20%(TiC + 2TiB₂) **c** composites

Fig. 9 Schematic drawing illustrates the formation of microstructure in Ni–Al–3Ti–B₄C system

reinforcements in NiAl intermetallic [11, 23, 27]. The forming process of the microstructure in Ni–Al–3Ti–B₄C system by method A is schematically illustrated in Fig. 9. The distribution of the mixed powders after pressing is shown in Fig. 9a. For this system, the contents of raw powers (3Ti + B₄C) would affect the heat release during the reactions between raw powders. It is known that the adiabatic combustion temperature of the 3Ti–B₄C system (3193 K) [28] is higher than that of NiAl (1911 K) [29]. The combustion temperature of Ni–Al–3Ti–B₄C system will be between 1911 and 3193 K, which is higher than the melting points of NiAl intermetallic and pure Ti. So the

higher content of 3Ti + B₄C would result in the increase of both the combustion temperature and the liquid content during the synthesis of composite by SHS process. Furthermore, the surface of solid particles of B₄C would be surrounded by the metal liquid at high temperature. Then the atoms of boron and carbon from the decomposition of B₄C solid particle react with Ti to form TiB₂ and TiC [30], respectively, as illustrated in Fig. 9b and c. In addition, the higher the contents of 3Ti + B₄C are, the higher the temperature and the longer the duration at high temperature would be. Thus, there is enough time and kinetic energy offered for the precipitation and growth of TiC and TiB₂

Fig. 10 Schematic drawing illustrates the formation of microstructure in Ni–Al–2TiB₂–TiC system

Fig. 11 SEM images showing the microstructures of NiAl–TiC–TiB₂ composites with different contents of (TiC + 2TiB₂): **a** B-10, **b** B-20

phases. As a result, the final morphologies of TiB₂ and TiC tend to be faceted growth, leading to rectangle, hexagon, and quasi-spherical shapes [31, 32], as shown in Fig. 9d. Moreover, during the decomposition of B₄C and reaction with Ti, TiC and TiB₂ would form on the surface of B₄C, and the NiAl liquid would fill in the vacancy part. This will be more clear in some regions with increasing content of 3Ti + B₄C (see in Figs. 4d, 5a and 9d).

The forming process of the microstructure in Ni–Al–2TiB₂–TiC system is clearly different from Ni–Al–3Ti–B₄C system, as illustrated in Fig. 10. Figure 10a shows the distribution of the raw powders after pressing. In this system, the added particles of 2TiB₂–TiC have not been involved in any reaction, only acting as a dilution to the reaction of Ni and Al [8, 29]. In addition, as the combustion temperature is higher than the melt point of NiAl

during the process of SHS [29], the NiAl must be melted during ignition (as shown in Fig. 10b). Hence, with the increasing content of the $\text{TiC} + 2\text{TiB}_2$, the heat which was absorbed by it would increase and the volume fraction of NiAl liquid would also decrease relatively. Moreover, the melting point of TiC and TiB_2 is much higher than NiAl. So during the solidification, the NiAl phase may nucleate at the surface of the solid TiC and TiB_2 particles. With further cooling and growth of NiAl grains, the TiC and TiB_2 particles would be rejected to the grain boundaries of NiAl. As a result, most of the TiC and TiB_2 particles are trapped by solidified NiAl grains and segregated to the boundaries, the others dispersed in the unmelted NiAl. At the end of solidification of NiAl phase, the TiC and TiB_2 particles mainly distributed along the NiAl grain boundaries, as illustrated in Fig. 10c, d. This reasoning is confirmed by the microstructural observation using SEM, see particles pointed by arrows 1 and 2 in Fig. 11a, b. In addition, a part of TiC and TiB_2 particles is pushed and jammed together, as pointed by arrow 3 in Fig. 11a. This resulted in the inhomogeneous distribution and severe segregation of TiC and TiB_2 particles in the composite.

5 Conclusions

- (1) In situ-formed and externally added TiC– TiB_2 in NiAl matrix composites were successfully fabricated by SHS technique. The synthetic method of TiC– TiB_2 had no effect on the phase composition, and all composites comprise NiAl, TiC, and TiB_2 phases.
- (2) TiC– TiB_2 ceramic particulates mainly distributed along NiAl grain boundaries and a small amount embedded within NiAl grains especially in the in situ-formed TiC– TiB_2 particles. The TiC– TiB_2 particles in situ formed in the NiAl matrix through the decomposition-precipitation mechanism were extremely fine and distributed uniformly. Meanwhile, externally added TiC– TiB_2 particles, which distributed inhomogeneously with severe agglomeration in NiAl matrix, formed following a pushed-trapped mode during the growth of NiAl grains.
- (3) The grains of NiAl matrix in the composites synthesized by the two methods have been both refined. The hardness of the NiAl matrix in the composites made by two methods is improved. But the improvement of the composites containing in situ-formed reinforcements is much significant than those with externally added reinforcements.

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