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Reinforcing and toughening of TiAl composites by doping Sm_2O_3

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Abstract: Al_2O_3/TiAl composites were fabricated by in-situ reaction synthesis using Ti, Al, TiO_2 and Sm_2O_3 as starting materials. Effect of the doping Sm_2O_3 on the microstructures and properties of the Al_2O_3/TiAl composites was analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and universal properties tests. The results show that the phases of the Sm_2O_3-doped composites are mainly composed of γ-TiAl/α_2-Ti_3Al matrix and reinforcing phases of Al_2O_3 and SmAl. The microstructures of Al_2O_3/TiAl composites are significantly refined with doping Sm_2O_3. Doping Sm_2O_3 has a positive effect on improving the mechanical properties of Al_2O_3/TiAl composites. When the Sm content is 5% (mass fraction), the flexural strength and fracture toughness reach the maximum values of 658.9 MPa and 10.13 MPa·$m^{1/2}$, respectively.

Key words: TiAl; Sm_2O_3; grain size; mechanical properties

1 Introduction

Titanium aluminides exhibit numerous attractive properties for high-temperature structural applications due to their high elastic modulus, low density, and good creep resistance to high temperatures [1]. A further increase of application may be accomplished through microstructural control and alloy modification [2−3]. Generally, coarse grain fully lamellar microstructures exhibit relatively poor tensile ductility and strength, but relative grain-refining near-γ or duplex microstructures show better tensile properties [4]. Therefore, controlling and refining microstructure is one way to attain ideal mechanical properties. Several routes are commonly used for this purpose, such as activation of selected phase transformations, wrought processing or addition of grain growth inhibitors [5].

There are different second-phase particles, such as TiB_2, SiC, TiC, Ti_2AlC and Al_2O_3. Al_2O_3 has been chosen as a ceramic reinforcement because of its advantageous thermo-mechanical behavior, inclusive of wear resistance, environmental stability, high temperature strength, and so on [6]. The ductility and strength can be improved by reducing grain size and lamellar spacing without compromising the fracture toughness and creep resistance. Rare earths (RE) are widely used in metallurgical fields, due to improved performance of sintering, heat-machining, mechanics, oxidation/corrosion and wear resistance by means of purifying, transformation and alloying processes [7].

Previous researches on TiAl intermetallic alloys were focused mainly on RE addition, but the effects of doping RE_2O_3 on TiAl were not studied in detail. In this work, Sm_2O_3 was added to the starting materials of Ti, Al, TiO_2 to modify the Al_2O_3/TiAl in situ composites. The effects of Sm_2O_3 addition on the microstructure and mechanical properties of the composites were investigated. Furthermore, the refined mechanism was also discussed.

2 Experimental

For the production of the Al_2O_3/TiAl composite, reactant samples were prepared from the mixture of Ti (Strem chemicals, 53 μm, 99.3% of purity), Al (Showa Chemical Co, 75 μm, 99% of purity), TiO_2 (0.5 μm, 99% of purity), and Sm_2O_3 (30 μm, 99.9% of purity) powders by the stoichiometry according to the following reaction:

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$$x\text{Ti}+(x+13)\text{Al}+3\text{TiO}_2+\text{Sm}_2\text{O}_3 = (x+3)\text{TiAl}+3\text{Al}_2\text{O}_3+2\text{SmAl}_2 \quad (1)$$

where the stoichiometric parameter x is 16.97, which represents the Al_2O_3 content is 12% (mass fraction) in the target TiAl-matrix composites, and the Sm mass fraction varies from 0 to 6%. Eight samples were designed in Table 1.

Table 1 Composition of samples (mass fraction, %)

Sample No.	Ti	Al	TiO_2	Sm_2O_3	Target Sm	Target Al_2O_3
0	47.84	38.06	14.11	−	−	12
1	48.13	38.3	14.24	0.23	0.2	12
2	48.09	38.36	14.22	0.58	0.5	12
3	48.00	38.47	14.20	1.16	1.0	12
4	47.83	38.7	14.15	2.32	2.0	12
5	47.65	38.92	14.09	3.48	3.0	12
6	47.48	39.14	14.03	4.64	4.0	12
7	47.31	39.37	14.00	5.80	5.0	12
8	47.14	39.59	13.94	6.96	6.0	12

The desired mixtures were ball milled in ethanol for 1 h. The mass ratio of ball to powder was 3:1, and the rotational velocity was kept at 800 r/min. Further processing included drying at 60 °C for 5 h and sieving through 75 μm-sieve. The reactive sintering of the as-milled powders was performed in a sintering furnace under vacuum less than 10^{-2} MPa. The compacted powder mixture was heated at a rate of 10 °C/min from room temperature to 500, 700, 900, 1 100, 1 200, 1 250 and 1 300 °C and held for 2 h, respectively, wherein the pressure was gradually increased to 35 MPa. Finally, the sample was cooled down in furnace to room temperature.

The phase composition of the fabricated samples was analyzed by an X-ray diffractmeter (Rigaku D/max 2000P) with Cu K_α radiation operating at 40 kV. The microstructure, fracture surfaces and crack propagation of the samples were investigated by scanning electron microscopy (SEM) (JSM−6700F SEM).

The Vickers hardness of Al_2O_3/TiAl composites was measured at room temperature on a HXD−1000 tester with a diamond indenter under 10 N for 15 s. The density measurements were performed via Archimedes principle. The samples were cut and ground into strip specimens with dimensions of 25 mm×4 mm×3 mm for measuring the three-point bending strength on a universal testing machine with a span of 25 mm at a cross-head speed of 5 mm/min at room temperature. The bending strength was calculated by the following equation:

$$\sigma=3PL/(2bh^2) \quad (2)$$

where P is the breaking load of the specimen, and L, b, and h denote the span, width, and height, respectively.

The fracture toughness was measured on the universal testing machine by using the single-edge notch beam (SEPB) method with specimen dimensions of 36 mm×4 mm×8 mm. The notch depth was 4 mm with ~0.15 mm in width. The crosshead speed was 0.05 mm/min, with a loading span of 30 mm. The fracture toughness, K_{IC}, was calculated by the following equation:

$$K_{IC}=Y\times 3PL\,a^{1/2}/(2bh^2) \quad (3)$$

where a is the notch length, and Y is a geometrical factor.

3 Results and discussion

Figure 1 shows the X-ray diffraction patterns of

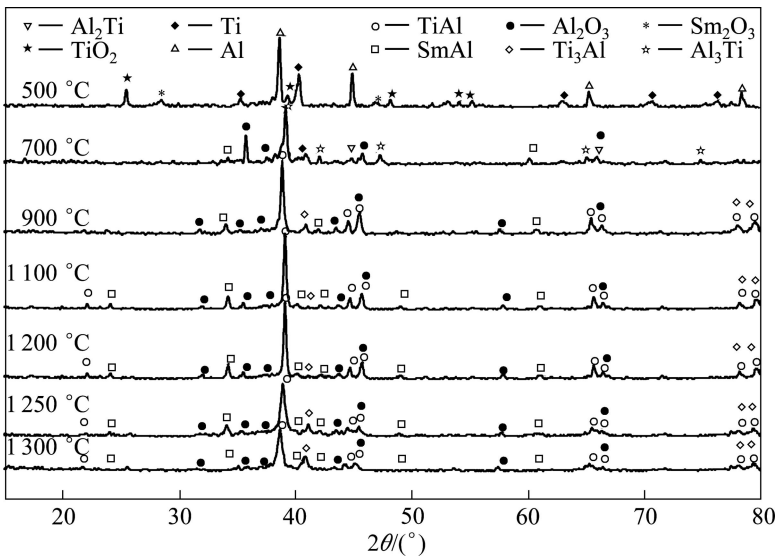

Fig. 1 XRD patterns of composites at various temperatures

Al_2O_3/TiAl composites with 5% Sm after being hot pressed at various temperatures for 2 h. According to XRD analysis, there is no reaction among Ti, Al, TiO_2 and Sm_2O_3 powders when the mixed powders are sintered at 500 °C for 2 h. When the temperatures is increased to 700 °C (higher than the melting points of Al), the as-sintered samples mainly consist of Al_3Ti and Al_2O_3 as two major phases together with a significantly smaller amount of Al_2Ti, SmAl and unreacted Ti phase.

When the temperatures is 800 °C, the values of free-energy change, $\Delta G_m^{\Theta}(T)=\Delta H_m^{\Theta}(T)-T\Delta S_m^{\Theta}(T)$, of reactions among Al，Sm and O_2 are as follows [8]:

$$\Delta G^{\Theta}_{Sm_2O_3}=-1\ 829.69-(-1\ 098.15\times 402.38\times 10^{-3})$$
$$=-1\ 387.82\ \text{kJ/mol} \quad (4)$$

$$\Delta G^{\Theta}_{Al_2O_3}=-1\ 583.99-(-319.23\times 10^{-3})\times(800+298.15)$$
$$=-1\ 233.43\ \text{kJ/mol} \quad (5)$$

According to the Gibbs free-energy change, there is no thermite reaction between Sm_2O_3 and Al, which indicates that the formation of SmAl is thermodynamically infeasible. However, Sm_2O_3 can decompose into [Sm] and [O] because of active effect of the massive reaction heat released by Ti and molten aluminum, which can affect the kinetics or the mechanism of reaction between Sm_2O_3 and Al, which leads to the formation of SmAl.

When the temperature is increased to 900 °C, the composite mainly consists of γ-TiAl, α_2-Ti_3Al, Al_2O_3 and SmAl phases. The presence of the above-mentioned phases in the composites samples confirms the feasibility of the following in-situ reactions:

$$3TiO_2+4Al=2Al_2O_3+3Ti \quad (6)$$

$$Sm_2O_3+4Al=Al_2O_3+2SmAl \quad (7)$$

$$4Ti+2Al=TiAl+Ti_3Al \quad (8)$$

When the temperature was increased from 900 to 1 250 °C, it can be found that there were no much changes in phase composition, but the TiAl diffraction peaks were weakened and broadened gradually; on the contrary, the Ti_3Al diffraction peaks were increased because some TiAl phase transformed to Ti_3Al phase and formed the duplex microstructures, which is beneficial to increasing the combination properties of Al_2O_3/TiAl composites [9].

Figure 2 presents the XRD patterns of the in-situ composite samples with different contents of Sm_2O_3 hot-pressed at 1 250 °C for 2 h. Compared with Sm_2O_3 free samples, the samples with Sm_2O_3 addition consisted of the same three major phases of γ-TiAl, α_2-Ti_3Al and Al_2O_3. But a significant smaller amount of SmAl phase was produced. Although it is hard to quantify the individual phases in the products, it is clear that the intensity of the SmAl diffraction peaks increases with the increase of the content of Sm_2O_3.

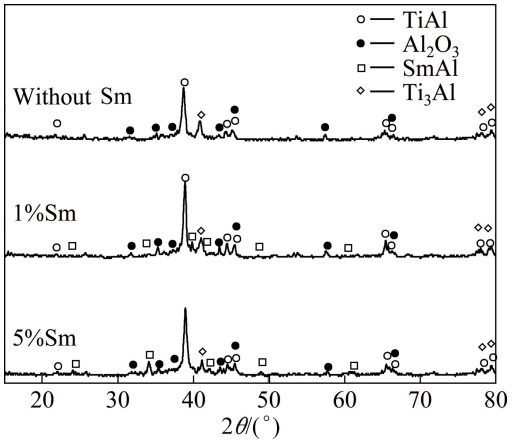

Fig. 2 XRD patterns of in-situ composites with various Sm_2O_3 contents

Figure 3 shows the typical fracture microstructures of the Al_2O_3/TiAl composites with various Sm_2O_3 contents after being hot-pressed at 1 250 °C for 2 h. The fracture microstructure of the composites is characterized by numerous brighter reinforcing phase of Al_2O_3 and black matrix phases of TiAl, Ti_3Al and SmAl. The fracture surface is uneven and few pores exist. The brighter areas present interpenetrating network structure. The Sm_2O_3 doping results in finer microstructure and more uniform distribution of Al_2O_3 particles without obvious agglomeration. It is attributed to Sm_2O_3 that the wettability between Al_2O_3 and TiAl increases because of its surface-active action [10].

Figure 3 shows that composites consist of single phase regions of γ-TiAl, lamellar regions of γ-TiAl+α_2-Ti_3Al with a dispersion of randomly oriented Al_2O_3 particles and SmAl distributing at grain boundaries, where most of the Al_2O_3 particles have smaller average grain size. These observations are found to be in agreement with the inferences drawn from the XRD studies. The average grain size of the composites with Sm_2O_3 addition was 0.3−0.5 μm. According to Ref. [11], the additions of other beta-stabilizing elements are beneficial to preventing peritectic growth. In this work, the addition of Sm_2O_3 hinders the growth of the TiAl matrix and Al_2O_3 grains and refines the grain size.

Figure 4 shows the crack propagation paths of the Al_2O_3/TiAl composites. Microstructures of the representative crack propagation paths reveal that variously complex toughening mechanisms can be found in the as-synthesized composite including extensive crack deflection, crack bridging, particle pullout, which mostly results from particles toughening effect [12].

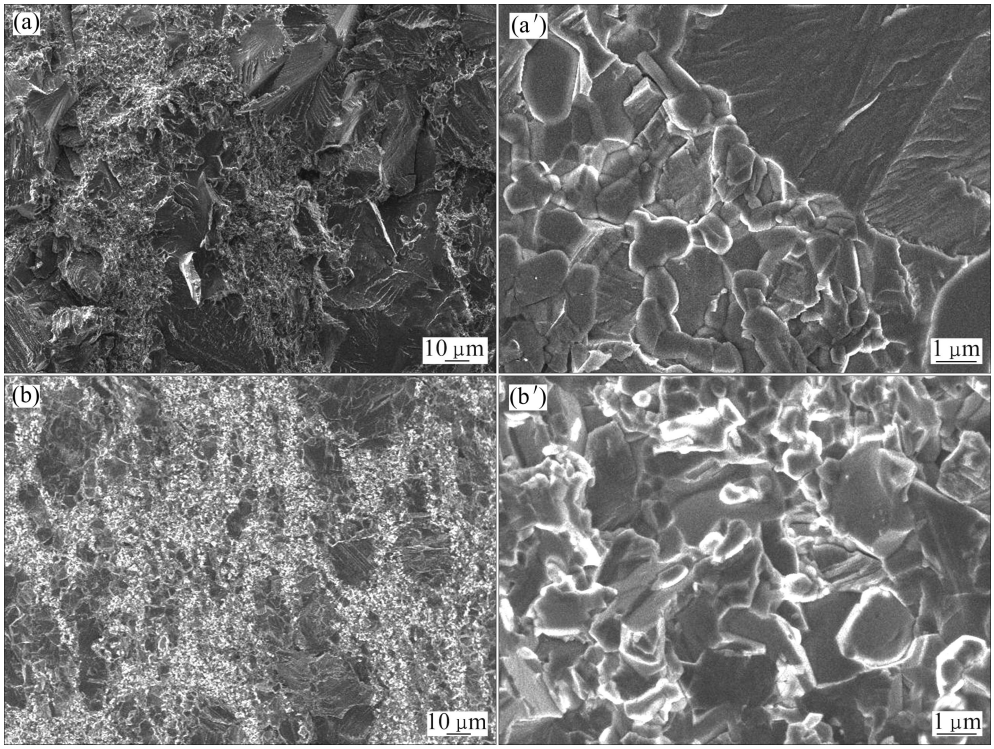

Fig. 3 Fracture microstructures of Al_2O_3/TiAl composites with various Sm_2O_3 contents: (a), (a′) Without Sm; (b), (b′) With 5%Sm

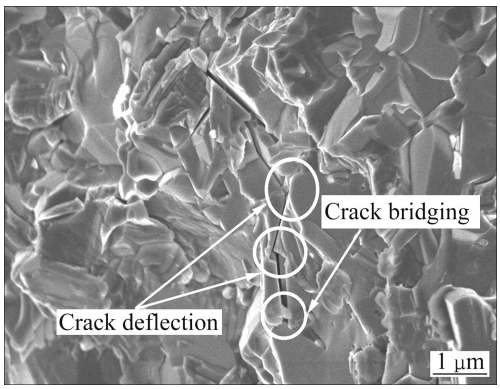

Fig. 4 Crack propagation paths of Al_2O_3/TiAl composites

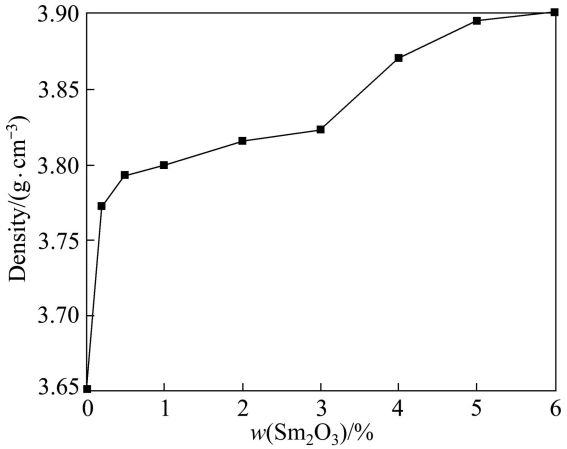

Fig. 5 Density of Al_2O_3/TiAl composite as function of Sm_2O_3 content

Figure 5 shows the density of the Al_2O_3/TiAl composite sintered at 1 250 °C for 2 h as a function of Sm_2O_3 content measured by the Archimedes method. The densities of Al_2O_3/TiAl increased steadily from 3.65 to 3.9 g/cm^3 with the Sm content increasing from 0.2% to 6%. Samples with the addition of Sm_2O_3 have higher densities due to their lower melting points [13], which increases densities of the TiAl-based composites. The second reason must be the higher densities of Sm_2O_3 itself, which also improves the densities of the composites. Finally, the densities of the composites increase due to the fine Al_2O_3 particles filling the pores.

Figure 6 presents the Vickers hardness of samples as a function of Sm_2O_3 content. A closer observation of the Vickers hardness data reveals that the hardness of the as-sintered composites goes up from HV_{10} 470 to HV_{10} 655.2 with the increase of Sm mass fraction from 0.2% to 6%. The increase of hardness can be correlated with the amount of SmAl reinforced phase. Meanwhile, the SmAl phases have a higher melting point and hardness than γ or α_2 phase [14], filling a part of the pores, which significantly increases the hardness of the composites.

As shown in Fig. 7, the variation trend of the fracture toughness is similar with that of the flexural strength. The fracture toughness and flexural strength increase with the increase of Sm mass fraction from 0.2% to 5%. With 5% Sm addition, the fracture toughness and flexural strength reach the maximum

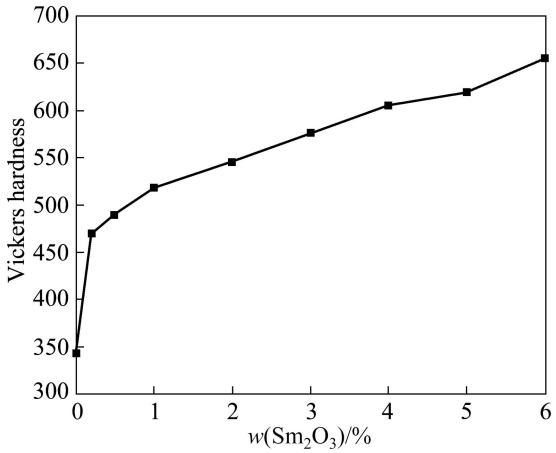

Fig. 6 Vickers hardness of products as function of Sm_2O_3 content

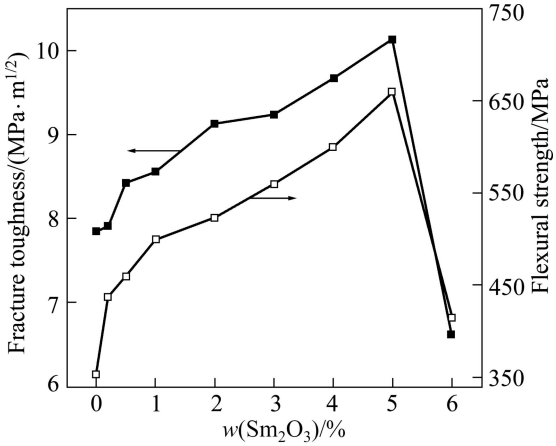

Fig. 7 Flexural strength and fracture toughness of products as function of Sm_2O_3 content

values of 10 MPa·m$^{1/2}$ and 659 MPa, respectively. When the mass fraction of Sm_2O_3 is further continuously increased over 5%, both the flexural strength and fracture toughness decrease. Referred to previous work [15], the strength of the composites generally increases with decreasing size of the reinforcements. The addition of Sm_2O_3 decreases the size of the reinforcements, which is beneficial for the improvement of the mechanical properties of the Al_2O_3/TiAl composites [16]. However, the fracture toughness and the flexural strength decrease rapidly with excess Sm_2O_3 addition due to the excessive formation of the brittle SmAl phase.

4 Conclusions

1) Al_2O_3/TiAl composites were fabricated by in-situ reaction synthesis using Ti, Al, TiO_2 and Sm_2O_3 as starting powders. The as-sintered samples mainly consist of α_2-Ti_3Al, γ-TiAl, Al_2O_3 and SmAl phases.

2) The grain size of TiAl matrix decreases with the addition of Sm_2O_3 due to the uniform distribution of the in situ formed fine Al_2O_3 particles. The densities of the composites increase gradually from 3.5 g/cm^3 to 3.9 g/cm^3 and Vickers hardness increases from 340 to 655 kg/mm^2 with increasing Sm content from 0 to 6%. Both the flexural strength and fracture toughness are modified and reach the maximum values of 659 MPa and 10 MPa·m$^{1/2}$ respectively when Sm_2O_3 mass fraction is 5%.

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Sm_2O_3 掺杂强韧化 TiAl 复合材料

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摘 要：以 Ti，Al，TiO_2 和 Sm_2O_3 为原料，利用原位合成法制备 Al_2O_3/TiAl 复合材料；并借助 XRD、SEM 和力学性能测试，研究 Sm_2O_3 掺杂对 Al_2O_3/TiAl 复合材料微观结构和力学性能的影响。结果表明：掺杂 Sm_2O_3 的 Al_2O_3/TiAl 复合材料由 γ-TiAl/α_2-Ti_3Al 基体相以及 Al_2O_3、SmAl 增强相组成；掺杂 Sm_2O_3 细化了复合材料的微观结构，改善了 TiAl 复合材料的力学性能；当 Sm 含量为 5%(质量分数)时，该复合材料的弯曲强度和断裂韧性达到最大，分别为 658.9 MPa 和 10.13 $MPa\cdot m^{1/2}$。

关键词：TiAl；Sm_2O_3；晶粒尺寸；力学性能

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