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Structure and morphology of Ti-Al composite powders treated by mechanical alloying

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Abstract: The evolution in microstructure and composition of the milled Ti-Al composite powder with different milling time were investigated. It shows that with the milling time increasing, the initial powder underwent a successive change in its morphology from a flattened shape (2 h) to a fine, equiaxed and uniform one (above 6 h). The milled Ti-Al composite powder was nanocrystalline with the average crystallite size of about 17 nm after milling for 8 h. The evolution mechanism of Ti-Al composite powder was elucidated. The Ti(Al) solid solution is formed through a gradual and progressive solution of Al into Ti lattice. By differential thermal analysis on the ignition temperature of the reaction between Ti and Al as a function of milling time, it indicates that mechanical milling of the powders significantly lowered the ignition temperature of the reaction by refining its Ti-Al composite structure.
Key words: TiAl; composite powder; mechanical milling

1 Introduction

TiAl-based alloys are important engineering materials with a great potential to replace nickel-based superalloys and titanium alloys applied in aerospace and automotive due to their high specific strength and stiffness, high strength retention at high temperature and high creep resistance at temperatures up to 800 °C [1−3]. At present, TiAl alloys have been gradually put into practical application such as exhaust valves, and the turbine superchargers used in automobile engine [4−5], and the turbine blades able to endure about 150 MPa stress at elevated temperatures [6]. However, the poor ductility at an ambient temperature and the low strength at an elevated temperature of TiAl alloy were significant limitations in broadening their practical application [7]. The ductility of TiAl intermetallic based alloys at room temperature can be improved by refining the microstructures of the alloys in terms of volume fraction of the α_2-Ti_3Al phase, and the structure and size of the lamellar colonies through heat treatment and composition modification [8]. It has also been demonstrated that an effective way of improving the formability and ductility of the material is refining near-gamma grains and/or the lamellar colonies [9−10].

Mechanical alloying (MA) at low temperature, as a non-equilibrium and solid-state powder processing technique, involves repeating, fracturing, cold-welding and re-welding of powder particles in a high-energy ball milling. Studies indicated that MA is capable of synthesizing a variety of equilibrium and non-equilibrium alloy phases, including supersaturated solid solutions, metastable crystalline phases, amorphous alloys and nanostructures [11]. MA is a feasible method for preparing in-situ particle reinforced composite powder [12−13]. Nevertheless, MA is a complex process and hence involves a large degree of uncertainty in obtaining desired phases and microstructures. Research efforts are still required so as to study the evolution of microstructure and property of the processed powder during ball milling.

2 Experimental

Ti powders (average particle size above 20 μm, 99.5% of molar fraction and Al powders 99.9% of molar fraction, average particle size about 25 μm) were used as experimentally raw materials. Powders above and stearic acid (1%, mass fraction) served as a process control agent were mixed homogenously by a planetary mill with stainless steel balls (6 and 10 mm in diameter) under argon (Ar) atmosphere. The milling time was 2, 4, 6 and 8 h at the speed of 400 r/min, respectively. The

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ratio of stainless steel ball to mixed powder was 20:1. The result of X-ray fluorescence spectroscopy shows that the contamination by Fe, Cr, and Mn from the milling tools was less than 0.2% (molar fraction) after 8 h milling.

Scanning electron microscopy (SEM, Hitachi S4000) was carried out to characterize the morphology of the milled powder. The structure of the as-milled powders was studied by X-ray diffraction (XRD) (Philips X-Pert system with Cu K_α radiation and a graphite monochromator). The sample holder was filled inside the glove box, covered with mylar film and put into a plastic box to protect the sample from atmospheric oxygen and moisture during transportation. The diffraction patterns were analyzed using the MDI Jade 5.0. Differential thermal analysis (DTA) was also conducted to study the transformation of reaction temperature during heating. The sample was placed in Al_2O_3 pans and heated to 800 °C at a rate of 20 °C/min in dynamic argon atmosphere.

3 Results and discussion

3.1 Microstructure characterization

The morphology and microstructure of the milled powders evolved for different milling time in the case of a high-energy ball milling (400 r/min) are illustrated in Figs. 1(a)−(d). The particle size distribution of powders becomes more homogeneous as ball milling was continued. The size of composite particles was smaller than 10 μm after 6 h ball milling. It was found that aluminum powders were refined first and emerged in irregular shapes and various sizes. However, titanium particles were mainly oval-shaped, as shown in Fig. 1(a). Figure 1(b) indicates the mixture particles became more equiaxed as high-energy ball milling proceeded. In the mean time, no deformation was observed yet. Cold welding and plastic deformation of the composite powder, essentially mixed by means of solid-state diffusion between titanium and aluminum atoms, were observed after milling for more than 6 h. The result above is also presented by Fig. 1(c) and Fig. 1(d), that is, only titanium particles enforced virtually by the insertion of the small aluminum particles were sufficiently plastically deformed and a layered structure and Ti-Al mixture were produced. The titanium particles which did not sink deeply enough within aluminum particles were little deformed and still presented a pure titanium core. Increasing the milling time to 8 h leads to flatten both

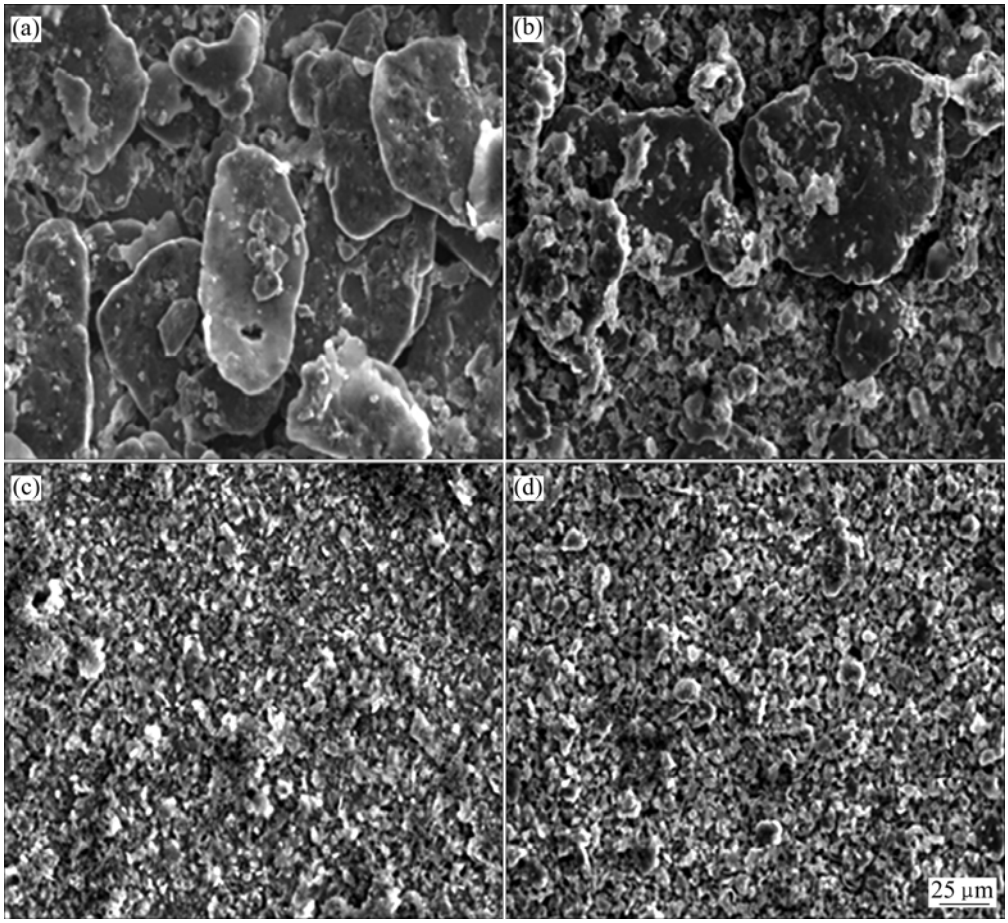

Fig. 1 SEM images of Ti-Al composite powders with different milling time: (a) 2 h; (b) 4 h; (c) 6 h; (d) 8 h

elemental particles in some areas and still coarsens some, as shown in Fig. 1(d). There was no obvious agglomeration in the milling process, which may relate to the process control agent.

3.2 XRD analysis

The X-ray diffraction patterns of Ti-Al composite powders milled for different milling time are shown in Fig. 2. It can be concluded that the XRD pattern of as-received powders is almost similar to that of 2−8 h-milled powders. However, the peak broadening and decreasing intensity were observed with the increase in milling time due to the decrease in crystallite size from 48 nm after 2 h to about 17 nm after 8 h. Shifts in titanium diffraction peaks towards higher angles were also observed, which was caused by the reduction in the lattice parameter and a distortion of Ti lattice because of Al diffusion.

It is also noticed from Fig. 2 that the diffraction peaks of Ti and Al slightly displaced toward higher angles as the milling duration increased, indicating the reduction in the lattice parameter attributed to a distortion of Ti lattice by Al diffusion and plastic deformation. It can be seen that Al has an extended solubility in Ti, while Ti has a limited solubility in Al at different temperatures from the widely accepted Ti-Al phase diagram. So as expected, Al predominantly diffused into Ti when both of them were treated by mechanical alloying. The peak broadening at this stage leads to the overlapping of peaks, so that the peaks could not be easily distinguished. Further milling caused the total intensity of peaks to decrease, which coincides with the appearance of an amorphous halo until the amorphization of Ti-Al powders was complete. It was noteworthy that the contribution of the grain boundary energy to the overall energy increases with decreasing grain size. This can lead to amorphization when the free energy of the intermetallic becomes higher than that of the amorphous phase. The XRD analysis revealed that the obtained homogeneous microstructure was comprised of bcc Ti-Al solid solution and deformed hcp Ti particles. The XRD patterns of the Ti-Al composite powders milled for 6 h and 8 h at 400 r/min have superimposed perfectly at similar 2θ angles. This indicates that there was not much structural change for composite powders milled for longer than 6 h.

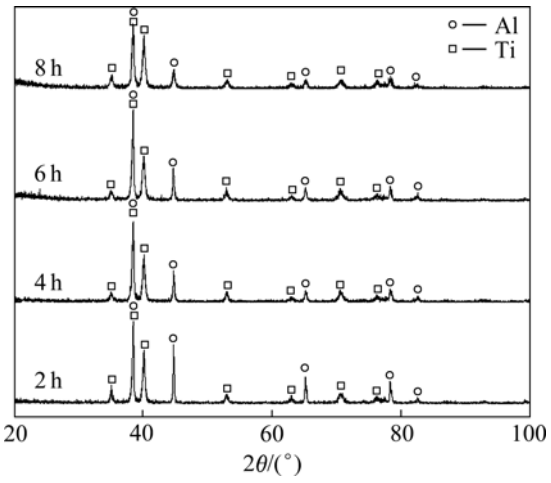

Fig. 2 XRD patterns of powders milled for different time

3.3 Thermal analysis

The thermal and reaction behaviors of milled Ti-Al composite powders were investigated by DTA. According to Fig. 3, it is obvious that major exothermic peaks appeared in the temperature range of 650−725 °C when the Ti-Al composite powders milled separately for 0, 2 h, and 8 h were heated up to 800 °C at 20 °C/min. The curve of 8 h-milled composite powders has no endothermic peak, which confirms that Al phases was completely consumed by the reactions occurring in the course of 8 h ball milling. It has been well established that the formation of Al_3Ti or supersaturated Al(Ti) solid solution depending on the scale of the Ti-Al diffusion couples was attributed by the first reaction between Ti and Al in Ti-Al composite powders [14−16]. TiAl was formed by the reaction between Al_3Ti or Al(Ti) solid solution and Ti after continuously heating. If Ti is still not fully consumed, TiAl will react with Ti to form Ti_3Al. The fact that Al melting did not occur during heating the composite powders was very important from powder metallurgy point of view. For excessive melting of Al and/or Al(Ti) phases during heating and sintering, a Ti-Al based powder compact can cause formation of pores in the consolidated material [17−18]. It has been found that the ignition temperature of the reactions between Ti and Al was significantly lowered by refining Ti-Al composite structure by means of mechanical milling.

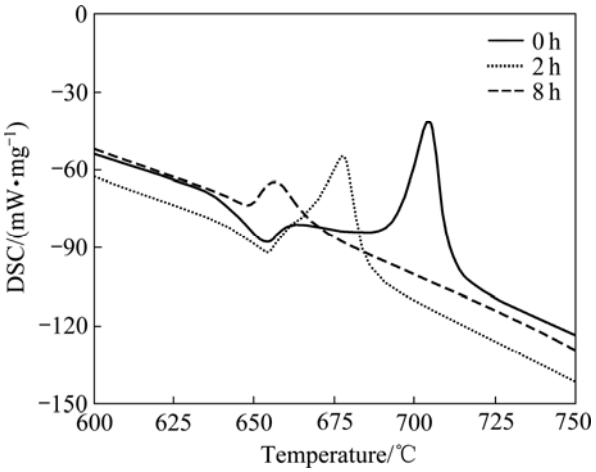

Fig. 3 DTA curves of Ti-Al powders with different milling time

4 Conclusions

1) Composite powders of Ti and Al were synthesized by high energy mechanical milling. The particles size is smaller than 10 μm after 6 h milling, and the crystallite size decreases from 48 nm after 2 h to about 17 nm after 8 h milling.

2) The aluminum powder is refined first during the ball-milling process. The composite particles become more equiaxed as mechanical milling proceeds. There is no obvious agglomeration for Ti and Al in the milling process, which may relate to the process control agent stearic acid. The decrease of the lattice parameters are attributed to a distortion of the Ti lattice caused by Al diffusion.

3) Calorimetric measurements, as a function of milling time, indicate that the ignition temperature of the reactions is significantly lowered by refining the Ti-Al composite structure. It is concluded that the thermal behavior of Ti-Al composite powders is highly influenced by the grain refinement.

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机械合金化 Ti-Al 复合粉末的结构及显微形貌

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摘　要：研究了不同球磨时间内 Ti-Al 复合粉末显微结构及成分的演变。随着球磨时间的延长，原始粉末的形貌发生了一系列变化，从球磨 2 h 的扁平状变为球磨 6 h 的细小的等轴状。球磨 8 h 后粉末的晶粒尺寸达到纳米级，平均约为 17 nm。对钛铝复合粉末的演化机理进行了分析。在球磨过程中，铝逐渐融入钛晶格形成钛的固溶体。球磨不同时间的粉末中钛铝反应的起始温度的差热分析表明，机械合金化细化了复合粉末，显著降低了钛、铝反应的起始温度。

关键词：TiAl；复合粉末；机械合金化

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