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Synthesis of amorphous Ti-Al alloys by mechanical alloying of elemental powders①

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[Abstract] Blended elemental powders with the nominal compositions (mole fraction, %) of $Ti_{54}Al_{46}$, $Ti_{52}Al_{48}$ and $Ti_{50}Al_{50}$ were mechanically alloyed in a planetary ball milling system for up to 100h. The structure evolution in these powders was characterized by scanning electron microscope, X-ray diffraction and differential thermal analysis techniques. It was found that elemental powders were progressively transformed into nanocrystalline Ti(Al) supersaturated solid solution, then into amorphous phase. With increasing Al content, the formation of a fully Ti(Al) supersaturated solid solution and amorphous phase were accelerated, which are attributed to the fine grain size. And the grain size condition for formation of amorphous phase in this system is ≤16 nm.

[Key wards] Ti-Al alloy; mechanical alloying; amorphisation
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1 INTRODUCTION

Titanium aluminides are attractive candidate materials for aerospace structural and engine applications, owing to their low density, high specific strength and modulus, excellent oxidation and corrosion resistances at least up to 800 ℃. However, a major obstacle for the use of these alloys is their ambient temperature brittleness and poor workability. Attempts to improve ductility of the alloys by addition of alloying elements and innovative heat treatments have limited progress[1, 2]. Recently, mechanical alloying (MA), by which elemental blends are milled to achieve alloying at the atomic level, is shown to be a powerful technique for producing supersaturated solid solutions, high melting intermetallics, amorphous phases and consequent improved properties[3, 4]. It is experimentally shown that titanium aluminides with a submicrocrystalline or nanocrystalline could be produced by consolidating mechanically alloyed Ti-Al powders[5~7]. When the grains were refined to submicroscale or nanoscale range, TiAl alloys would exhibit an improved ductility at room temperature and a considerable decrease in temperature for superplastic forming. Therefore, it is useful to investigate the mechanical alloying process of Ti-Al system.

There were many investigations on the constitution and structure of mechanically alloyed Ti-Al alloys[8~11]. However, the results differed depending on the condition of experiments. The intent of this paper is to study the MA of Ti-Al alloy containing 46%, 48% and 50% Al(mole fraction), and to analyze the results on the formation of the amorphous phase in this alloy system.

2 EXPERIMENTAL

Commercial metal powder of Ti and Al (< 150 μm, > 99%) were used to produce TiAl based alloys. Before mechanical alloying, the powders with the following nominal compositions were blended: $Ti_{54}Al_{46}$, $Ti_{52}Al_{48}$, $Ti_{50}Al_{50}$. The MA process was carried out in a planetary ball milling system with chromium steel vials and cemented carbide balls (8.5 mm in diameter). The ball-to-powder mass ratio was 15∶1. In order to prevent excessive welding of the particles to the balls and the inner walls of the vial, 2% (mass fraction) stearic acid was used as PCA. Powders and PCA were loaded in the vial inside a glovebox kept under an atmosphere of purified Ar gas, and an O-ring seal was used to maintain the Ar atmosphere. During milling, the speed of the vial was 450 r/min for the periods up to 100 h. Small amount of powders were taken out from the container after periodic pause of milling for analysis.

The morphology of mechanically alloyed powders was examined by scanning electron microscopy. The structure of powders was analyzed by X-ray diffractometry (XRD) using CoK_α at 50 mV and 100 mA. From the XRD patterns, the grain size of powders and the internal strain of lattice were estimated using the method introduced in Ref.[4]. The phase formation in mechanically alloyed powder was also analyzed by differential thermal analyses (DTA) at a heating

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rate of 10 ℃/min, where powders were heated under flowing purified Ar.

3 RESULTS

3.1 Morphological evolution

The premixed powders experienced a characteristic change in particle size and shape during milling process. Fig. 1 illustrates the change of particle size with milling time for three powders. At the early stage, the particle size increased slightly, then decreased with further milling, and reached a relatively stable particle size at the late stage. For $Ti_{54}Al_{46}$ and $Ti_{52}Al_{48}$ alloys, the stable particle size was achieved after 60 h milling. However, for $Ti_{50}Al_{50}$ alloy, the stable particle size was obtained only after 40 h milling.

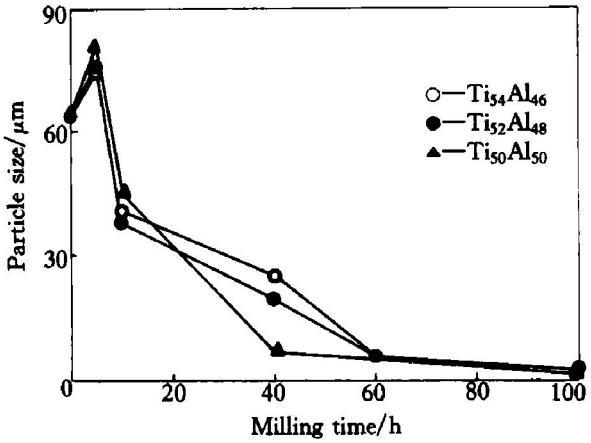

Fig. 1 Change of particle size during milling in $Ti_{54}Al_{46}$, $Ti_{52}Al_{48}$, $Ti_{50}Al_{50}$ alloys

Fig. 2 illustrates the change of particle morphology during milling process for $Ti_{54}Al_{46}$ powders. The change rule of morphology for $Ti_{52}Al_{48}$ and $Ti_{50}Al_{50}$ powders is similar to that for $Ti_{54}Al_{46}$ powders. In the early stage, powders are irregular and platelike, and the distribution of particle size is uneven (as shown in Fig. 2(a) and (b)). With increasing milling time, the powders changed into smaller equiaxed particles, and the distribution of particle size became narrow. From Fig. 2, it was also observed that with the increase of milling time, the plastic deformation of particle surface decayed gradually, therefore, the particles became harder and the fracture of particles became easier.

3.2 Structure evolution

The XRD spectra of $Ti_{54}Al_{46}$, $Ti_{52}Al_{48}$, $Ti_{50}Al_{50}$ powders milled for different time are shown in Fig. 3, Fig. 4 and Fig. 5, respectively. For starting powders, only sharp diffraction peaks of Ti and Al can be seen. These Ti and Al peaks are weakened and broadened with increasing milling time. The weakening of Ti

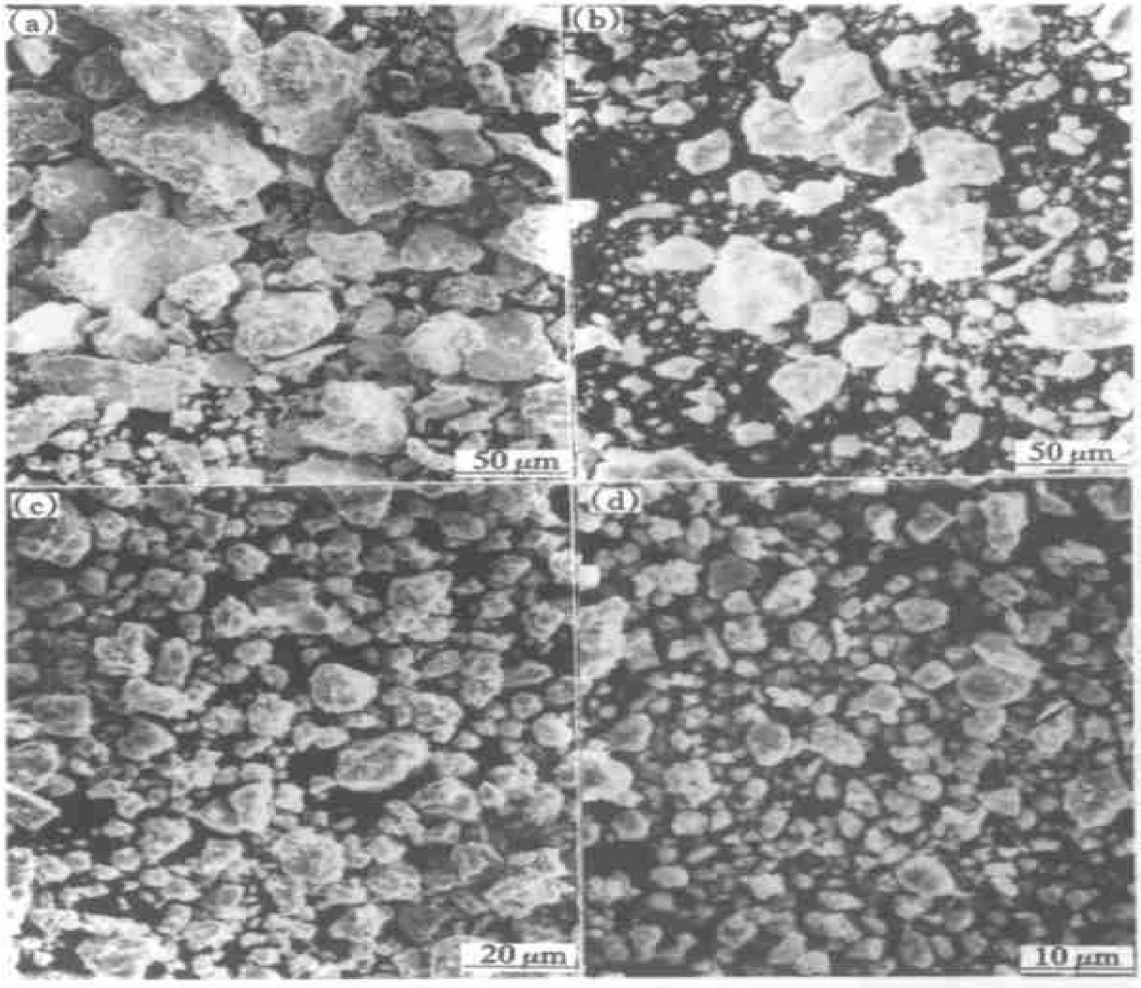

Fig. 2 Particle morphology of $Ti_{54}Al_{46}$ alloy powders milled for different time
(a) —10 h; (b) —40 h; (c) —60 h; (d) —100 h

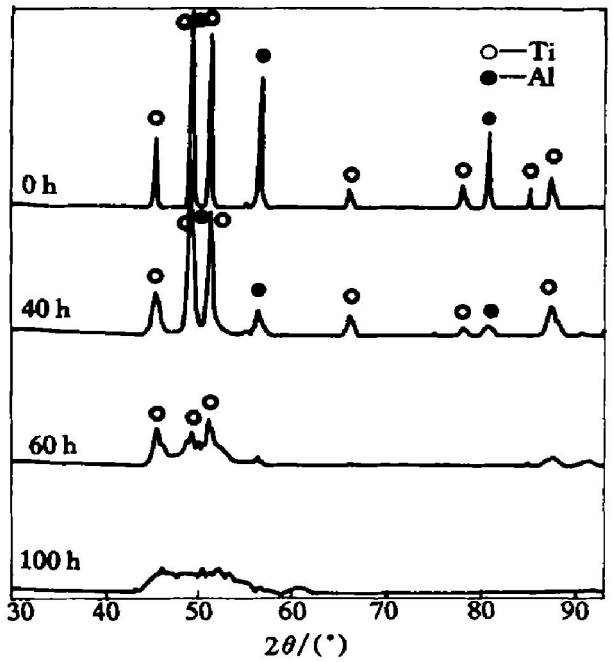

Fig. 3 XRD spectra of $Ti_{54}Al_{46}$ alloy powder milled for different time

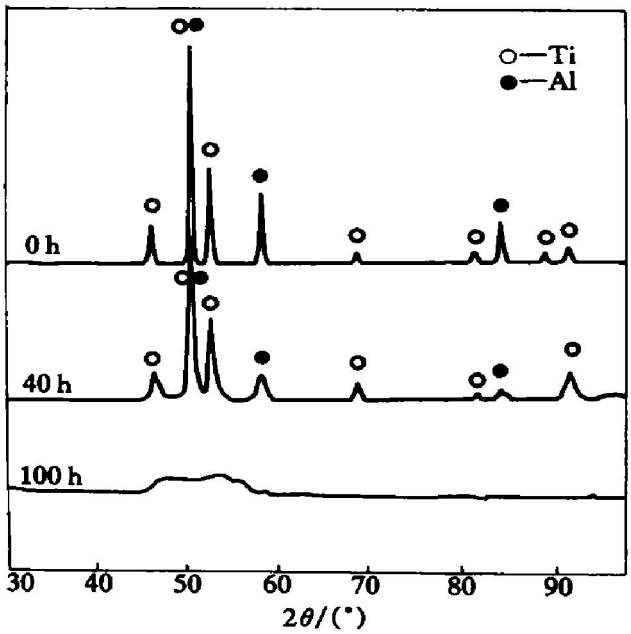

Fig. 4 XRD spectra of $Ti_{52}Al_{48}$ alloy powder milled for different time

and Al peaks indicates that dissolution due to interdiffusion between Ti and Al occurred during milling, whilst the broadening of these peaks indicates the decrease of the effective grain size and the increase of the internal strain. The change of grain size and lattice strain of as-milled powders is shown in Table 1. It is observed that in the process of milling, the grain size of powders decreased to nanoscale and the lattice strain of powders increased in the early stage, then decreased with decreasing grain size.

After certain period milling, only peaks of a hexagonal solid solution are observed in XRD spectra, and the lattice parameters of the solid solution phase changed slightly[8]. The hexagonal solid solution formation time for $Ti_{54}Al_{46}$ is 60 h, and for $Ti_{50}Al_{50}$ is

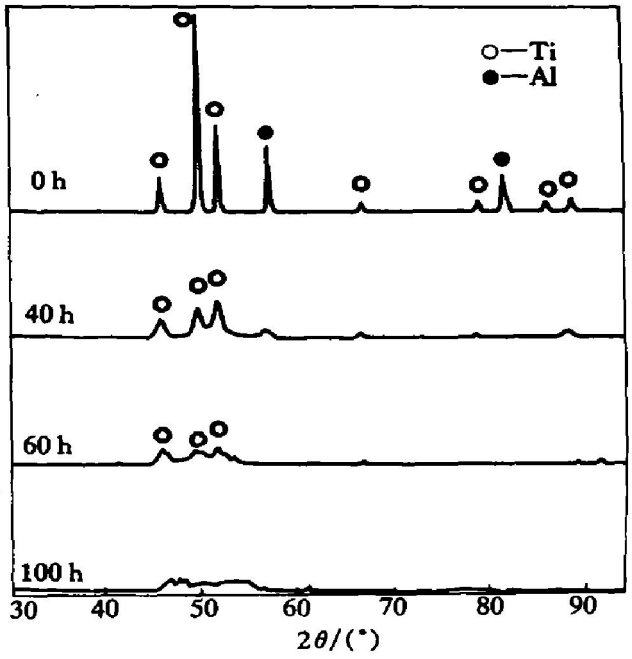

Fig. 5 XRD spectra of $Ti_{50}Al_{50}$ alloy powder milled for different time

Table 1 Change of grain size and lattice strain of as-milled powders in TiAl alloys

Alloy	Milling time/ h	Grain size/ nm	Lattice strain/ 10^{-4}
$Ti_{54}Al_{46}$	0	112.2	4.4
	30	70.4	28.9
	40	53.2	26.3
	60	15.0	16.9
$Ti_{52}Al_{48}$	0	112.2	4.4
	30	61.2	23.2
	40	38.9	18.4
	60	14.8	15.2
$Ti_{50}Al_{50}$	0	112.2	4.4
	30	33.4	17.6
	40	16.0	5.3
	60	12.2	5.0

40 h. This suggests that in that time all aluminum has dissolved in titanium to form an HCP supersaturated solid solution. At the same time, in XRD spectra, a broad amorphous peak was observed. After 100 h milling, peaks of Ti(Al) solid solution disappeared completely, and only a big broad amorphous peak remained.

The broad amorphous patterns may be resulted from a truly amorphous phase or an extremely fine grained crystalline material. To distinguish what the broad peak is, differential thermal analysis (DTA) combined with X-ray diffractometry was used to distinguish this phase. If the material is amorphous,

DTA result can show the presence of an exothermic peak when heating the sample, indicating that crystallization of the amorphous phase. If the material is extremely fine grained, only grain growth can occur on heating, in this case, a monotonically decreasing isothermal signal will be observed in the DTA curve. Fig. 6 shows DTA diagram of $Ti_{50}Al_{50}$ alloy for 100 h milling. It can be seen that there exists a exothermic peak in the temperature range from 660 ℃ to 730 ℃. Considering the results of X-ray diffraction, it was deduced that the exothermic reaction must be crystallization reaction of the amorphous phase.

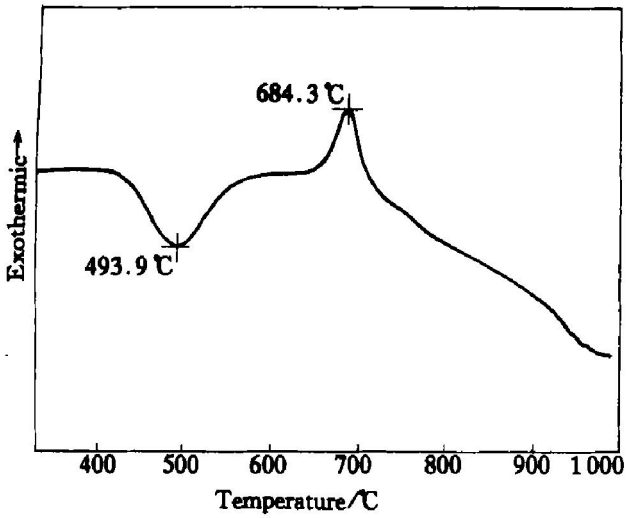

Fig. 6 DTA diagram of $Ti_{50}Al_{50}$ alloy powder for 100 h milling

4 DISCUSSION

It has been shown above that, during milling of Ti-Al system for 100h, an amorphous phase was formed by solid state amorphisation (SSA), and Al content affected this process greatly.

For any transformation, a driving force is required. The thermodynamic condition for SSA by MA is that the free energy of the amorphous phase must be lower than that of the initial pure metal mixture and the terminal solid solutions in that system. Generally, the temperature rising during milling is not high, so, the ΔS_{mix} can be neglected as its contribution to the free energy is found to be negligible in comparison with the contribution of ΔH_{mix}. Thus, the driving force for amorphisation comes mainly from the enthalpy contribution. Using the model of Miedema and his coworkers[12], the formation enthalpies of various competing phases, e. g. a solid solution or an amorphous phase, can be calculated:

$$\Delta H_{(\text{solid solution})} = \Delta H_{chem} + \Delta H_{elast} + \Delta H_{struct} \quad (1)$$

where ΔH_{chem} is the chemical contribution due to the mixing of atoms of two different metal, ΔH_{elast} is the elastic contribution due to the atomic size mismatch and ΔH_{struct} represents the lattice stability variation as a function of the average number of valence electrons per atom. According to this model, it has been calculated that the amorphous phase in the Ti-Al system has a much lower enthalpy than the elemental mixture of titanium and aluminum[9].

Another requirement for the amorphous phase to form is that there should be a large difference between the diffusivity of the two components involved. When $D_{(A\text{ in }B)} \gg D_{(B\text{ in }A)}$, the amorphous phase can grow at sufficiently low temperature where there is no possibility of nucleation and growth of intermetallic compounds. For Ti-Al system, the diffusivity of aluminum in α-Ti at room temperature is 1.06×10^{-21} cm^2/s and that of titanium in aluminum is 2.9×10^{-23} cm^2/s. Therefore, aluminum is a faster diffuser in α-Ti than that of titanium in aluminum. Both the thermodynamic and the kinetic requirements are satisfied for amorphous phase formation in the Ti-Al system. Several investigators have reported the glass-forming range of Ti-Al alloy is containing 20% ~ 90% Al (mole fraction)[4]. So in Ti-Al alloy with 46% ~ 50% Al, it is possible to form an amorphous phase.

During milling process, heavy deformation occurred, which resulted in the generation of large amounts of defects, including dislocations, vacancies, stacking faults, and grain boundaries. These defects play a key role in the transformation during milling. They can increase the free energy of as-milled powders, which aids in amorphisation process. Comparing with $Ti_{54}Al_{46}$ and $Ti_{52}Al_{48}$, $Ti_{50}Al_{50}$ powders have more grain boundaries (due to the smaller grain size) after 40 h milling, it had been proved that refining grain size to a critical limit is the key factor for the formation of amorphous phase[12]. The increased grain boundaries not only enhanced the interfacial energy, but also accelerated the diffusion of element. It is known that the diffusion coefficient of an element at grain boundary is 20 times faster than that in lattice. So, in $Ti_{50}Al_{50}$ powders, the amorphisation process was accelerated. But the reason why the slight change of Al content from 46% to 50% affected the structure of milled Ti-Al system so greatly is unknown. Tokizane et al[13] reported a resemble result that the Ti-rich Ti-Al MA powder (< 50% Al) milled for 920 ks were consisted mainly of Al supersaturated α-Ti nanocrystals, however, the Ti-50% Al and Ti-52% Al MA powders milled for the same time were composed mainly of an amorphous phase.

5 CONCLUSIONS

1) A fully amorphous phase was formed in the $Ti_{54}Al_{46}$, $Ti_{52}Al_{48}$ and $Ti_{50}Al_{50}$ alloys in mechanical

alloying process for 100h milling, following the formation of nanocrystalline Ti(Al) supersaturated solid solution.

2) Compared with $Ti_{54}Al_{46}$ and $Ti_{52}Al_{48}$ alloys, the slight increase of Al content in $Ti_{50}Al_{50}$ alloy resulted in the accelerating refining process of grain size, therefore shorten the formation time of nanocrystalline Ti(Al) supersaturated solid solution and amorphous phase.

3) In Ti-Al alloys, the grain size condition for formation of amorphous phase is $\leqslant$16 nm.

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