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Structural and phase formation of TiAl alloys synthesized by mechanical alloying and heat treatment

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Abstract

Mechanical alloying (MA) of Ti-50%Al (molar fraction) powder by using Planetary ball milling equipment, have been successfully refine the crystallite size and produced TiAl nano-alloys. The characteristics of the powder samples, including composition, surface morphology and microstructure, were investigated by using X-ray diffraction and field emission scanning electron microscopy (FESEM) coupled with Energy-dispersive X-ray spectroscopy (EDX). Mechanical alloying of elemental Ti and Al powder mixture resulting in the formation of Ti(Al) solid solution which exhibits a formation of TiAl phase after 40 h of milling. Crystallite size refinement by MA shows a great reduction from 70nm, down to minimum of 21nm after 100h of milling. Subsequent heat treatment of powder milled for 80 h exhibits the formation of a mixture of mainly α2-Ti_3Al plus γ-TiAl phases. On the other hand, 100h milled powder exhibits the formation of a major γ-TiAl with α2-Ti_3Al and a minor reflection of $TiAl_3$ phases. The crystallite size of heat treated powder are varies and exhibits a grain growth after 40h of mechanical alloying process as a result of multiple phases formation.

Keywords: TiAl intermetallics; Mechanical alloying; Nanostructured materials.

1. Introduction

Titanium aluminides (TiAl) intermetallics have long been considered as a very promising alloy for high-temperature structural material particularly in replacing nickel based superalloys [1-2]. In the past 20 years, their attractive properties that have the potential to enable the high temperature aerospace and automotive applications have attracted immense efforts in the development of novel TiAl intermetallics with the advantage of a good combination of excellent properties and hot workability. Equipped with the combination of low density (3.9g/cm^3), high strength to weight ratio up to 1000 MPa that can be retained at temperatures up to 700^{o}C, high specific stiffness, substantial resistance to oxidation and good creep properties up to 900°C [3-5], the application of parts and components made of TiAl intermetallics, is expected to reduce the structural weight by

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20–30% [6-7]. The advantages of this utilization of superior low density materials will contribute to fuel savings and consequently the reduction of CO_2 emissions [8-9].

The attractive properties of TiAl intermetallics somehow, were outweighed by their low ductility and difficulties in processing and machining at room temperature, which crippled the alloys from being commercially used [10-12]. Hence, deeper understanding of their phase formation, microstructure, micro alloying, deformation mechanisms and advances in manufacturing technologies are among the critical point to be focused in order to enable the commercialization of TiAl intermetallics in the future [13]. Recent researches have focused on the production of ultrafine grained TiAl intermetallics based alloys in attempts to improve ductility [13-16]. Powder metallurgy via mechanical alloying (MA) process is a promising alternative to fabricate ultrafine grained materials with controlled composition which enables the production of homogenous TiAl nano structured alloys with desired properties [17-18]. Thus, the process appears to be a very promising technique as it not only have the ability to refine the microstructural but also for obtaining materials of high structural homogeneity which latter have the improved mechanical properties [19-20].

In this present work, the fabrication of TiAl intermetallics through solid phase transformation and a massive crystallite refinement to nano meter range via mechanical alloying has been investigate. In addition the utilization of heat treatment in phase transformation and grain growth were also studied. Some perspective of the requirements to optimize the mechanical alloying and heat treatment conditions and parameters were also discussed by comparisons made between the properties and microstructures of samples produced from Ti and Al elemental powders.

2. Experimental

Elemental Al (99.97%) and Ti (99.5%) powders were used as the starting feed materials. The powders were weighted and mixed in the stoichiometric composition of Ti-50at.%Al (molar fraction) before loaded into the milling jar (250 ml) made of tungsten carbide (WC). Mechanical alloying processes were carried out by using Retsch PM 100 Planetary ball mill. For each batch, 5 grams of the powder mixture were used. WC balls with a diameter of 10 mm were used as milling media. The ball to powder weight ratio were kept approximately at 20:1 throughout the process. The jar then were clamped and sealed with rubber “o” ring and back filled with purified Argon gas (99.9%) in order to prevent contamination from the atmosphere. The rotation speed is set at 300 rpm with interval time at every 5 minutes. The millings were stopped at specific time and small amounts of powder were taken out for characterizations. Process control agent (PCA) such as hexane or wax which minimize the sticking of the powders to the milling tools, was not added in order to prevent additional contamination. The milling set up used are listed in Table 1.

Table 1: Mechanical alloying parameters and conditions for Ti50%Al powders

Parameters	Conditions
Milling jar	Tungsten Carbide, WC (250ml)
Grinding balls	Tungsten Carbide, WC (ø10mm)
Starting powder	Ti, 100 mesh (99.5% purity), Al (99.97% purity)
Rotation speed	300 rpm
Milling duration	Up to 100 hours
Ball-to-powder mass ratio	20:1
Environment	Ar (99.9% purity)

The surface morphology and microstructure of the powder were characterized by Joel JSM 7800F field emission scanning electron microscopy (FESEM) at an accelerating voltage of 10 kV coupled with Oxford X-Max energy dispersive X-ray spectrometer (EDX). Rigaku Minitron X-ray diffractometer, with Cu Kα radiation (λ = 1.54062 A°) were used to determined the structure and chemical compositions of the powders. Step scanning of 0.02 degree and 5 second of preset time mode from 20 to 80θ were used in order to precisely calculate the crystallite size and the lattice strain of the mechanically alloyed powders. Scherrer equation was use to estimate the crystallite size D from the line broadening of the x-ray diffraction profiles data:

$$D = 0.9\lambda/\beta\cos\Theta$$

Where, D is the mean crystallite size, λ is the CuK_α wave length of X-ray, Θ is the diffraction angles and β is the full width at half maximum (FWHM) of the XRD peaks.

$$\beta = (\beta_M^2 - \beta_I^2)^{1/2}$$

Where, β_M is the full width at half maximum (FWHM) and β_I is the correction factor for instrument broadening.

In order to study the phase transformation under heat treatment, the powders were put under controlled thermal load in a furnace at a rate of 10°C/min to the final temperature of 1000°C. Upon heating, the air in the dilatometer was flushed out by pure Argon (99.9%) to prevent excessive oxidation during heating. The age hardening was performed by kept the furnace at 1000°C for 2 hours before furnace cooled at a rate of 20°C/min.

3. Results and Discussion

3.1. Phase Evolution of Ti50%Al Powders

3.1.1 XRD and EDX Results during Mechanical Alloying Process

The evolutions of Ti50%Al powders mixture during mechanical alloying process were followed through by XRD. The XRD spectrums at different times of mechanical alloying process are shown in Fig. 1. As shown, the spectrums of the initial powder mixture

displayed a sharp Bragg diffraction peaks of Ti(hcp) and Al(fcc) with high intensity. Prolonged milling has resulted in a remarkable change of the XRD patterns, with Ti and Al peaks gradually becoming broader and the intensity decreasing dramatically after 100 h of milling. The peak broadening represents a reduction in crystallite size and an inducement of strain in the mechanical alloyed powder particles. A comparison of the principal Ti(1,0,1) and Al(1,1,1) peaks in the XRD patterns obtained for the different stages of milling indicated an apparent shift for the diffraction peaks to higher angle side. In most cases, the position of principal peak of Ti at $2\theta = 40.165^{o}$ were shifting gradually to $2\theta = 40.37^{o}$ angle, whilst the position of Al principal peak at $2\theta = 38.491^{o}$, shifts towards angle of $2\theta = 38.712^{o}$ as shown in Table 2. These peaks shifting indicate that the inter-diffusion between different atoms has occurred and Ti(Al) solid solution is formed.

The equilibrium solubility of Al in Ti at room temperature is only 0.5%, and solubility of Ti in Al is almost nil. However, in the mechanical alloying process, 10–60% Al can be dissolved in Ti, and in contrast, up to 36% of Ti can be dissolved in Al [21]. The phase formation during mechanical alloying occurs via solid state diffusion of elements. During the milling process, Al dissolved into Ti to form supersaturated solid solution. The fact that ball milling of pure metal powders produces only a line broadening, the shifting of the peak can be attributed to a lowering of lattice parameter of Ti due to the diffusion of Al, promoting the formation of Ti(Al) solid solution. Therefore, considerable solid solubility extensions were achieved by mechanical alloying alone.

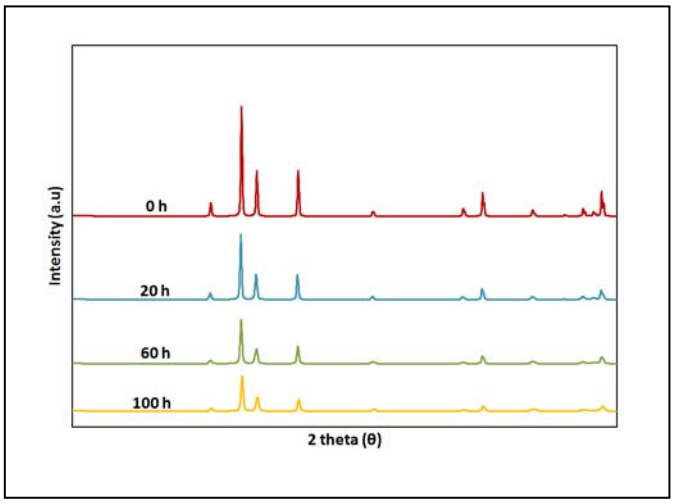

Fig. 1: X-ray spectrum of Ti50%Al powders at various milling duration.

Table 2: Principal peak at 2θ of Ti and Al at various milling duration

Miling Duration	Ti, Principal Peak	Al, Principal Peak
	(2θ)	
10hr	40.165	38.491
20hr	40.216	38.546
40hr	40.267	38.644
60hr	40.339	38.668
80hr	40.155	38.455
100hr	40.37	38.712

From the results obtained, it can be deduced that Ti(Al) solid solution has been formed by mechanical alloying process where its behaviour is strongly depends on the durations of the mechanical alloying process. In general, the Ti and Al peaks are weakened and broadened with increased in milling time to form a solid solution in the final states of milling at 100h. The gradual broadening of Ti and Al peaks, suggests an increase of strain in the internal crystallite or a decrease in the effective crystallite size, or both. This is proved by the estimation from Scherrer equation made by the data obtained from the Full Width at Half Maximum (FWHM) of XRD pattern. As shown in Fig. 2, a crystallite refinement of Ti-50%Al powders to nano size range occurred after 10h of milling with a great reduction from 70nm of the initial powder mixture to 21nm after 100h as a result of mechanical alloying process.

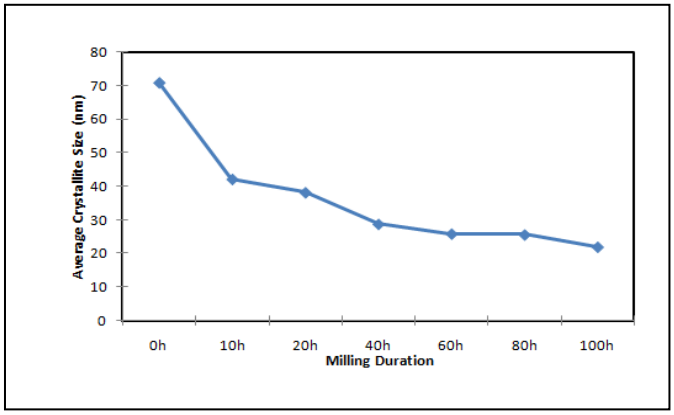

Fig. 2: Average crystallite size of Ti50%Al powder at various milling duration.

The gradual weakening of Ti and Al peaks during milling process from 0 h to 100 h suggested that dissolution due to inter-diffusion between the Ti and Al elements has occurred. This is supported by Energy Dispersive X-ray (EDX) analyses of the powders milled for 40h and 100h which indicated with prolonged milling, the contents of Al and Ti in particles were close to the initial composition respectively at room temperature. The *A* area of the micrograph given in Fig. 3 and in Fig. 4, confirmed that the likely phases of TiAl and $TiAl_3$ were identified amongst powder particles of 40h milled powder and TiAl phase for 100h milled powder. The EDX results obtained are in good agreement with XRD analysis, where the position of the principal peaks of both samples were close to the principal peaks of TiAl of $2\theta = 38.69^{o}$.

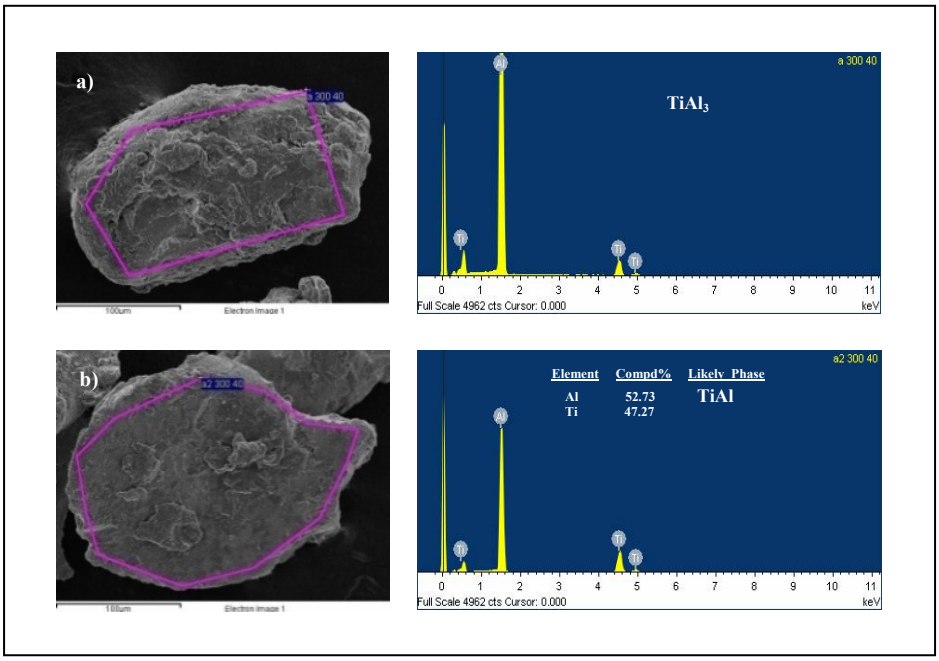

Fig. 3: FESEM image and EDX spectrum of Ti50%Al powder at 40h of milling duration with (a) $TiAl_3$ and (b) TiAl phase.

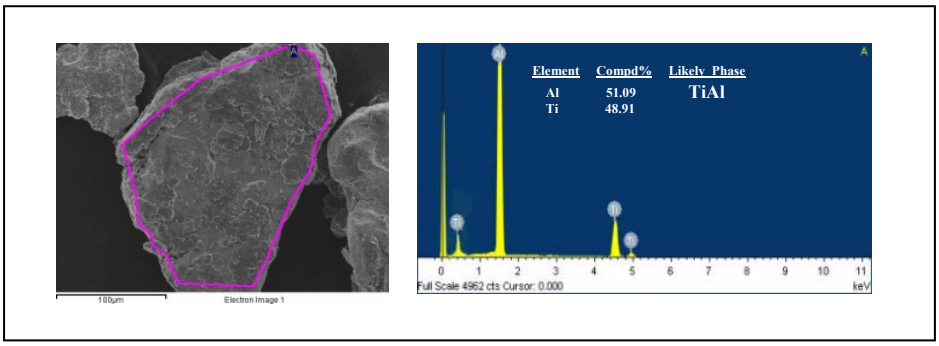

Fig. 4: FESEM image and EDX spectrum of Ti50%Al powder at 100 h of milling duration with TiAl phase.

3.1.2 XRD and EDX Results after Heat Treatment Process

The maximum solid solubility of Al in Ti was depending on the heating temperature. The solubility of Al in Ti at a temperature of 1100^{o}C is about 20%, and at a temperature of 1500^{o}C is about 50% [22]. In this present work, powder sample were heated to 1000^{o}C at a rate of 10^{o}C/min and kept for 2 hours before cooled down at a rate of 20^{o}C/min to room temperature. Fig. 5 shows the XRD spectrums of 80h Ti50%Al milled powder and Fig. 6 shows the XRD results of 100h milled powder before and after the subsequent heat treatment. The XRD result shows that the initial Ti50%Al powder precursor has changed into a mixture of high-temperature phases and a relatively stable phase structure after heat treated. As observed (not shown), the formation of Al_2Ti has occurred in powder milled for 40h and 60h as those samples exhibit almost similar DTA profile. In meanwhile, powder milled for 80h, a mixture of α2-Ti_3Al and γ-TiAl was formed which explain the lowest

temperature profile obtained. At longer milling duration of 100h, three equilibrium compounds, with major phase of γ-TiAl and a reflection of α2-Ti_3Al and minor $TiAl_3$ were obtained. The XRD results obtained are in good agreement with EDX analysis, where the particles component of heat treated 100h powders consist of γ-TiAl phase as shown in Fig. 7.

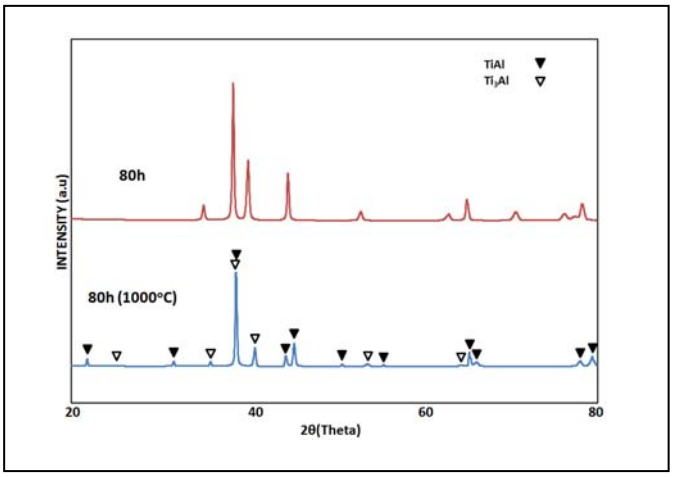

Fig. 5: X-ray spectrum of 80h milled Ti50%Al powders before and after heat treatment.

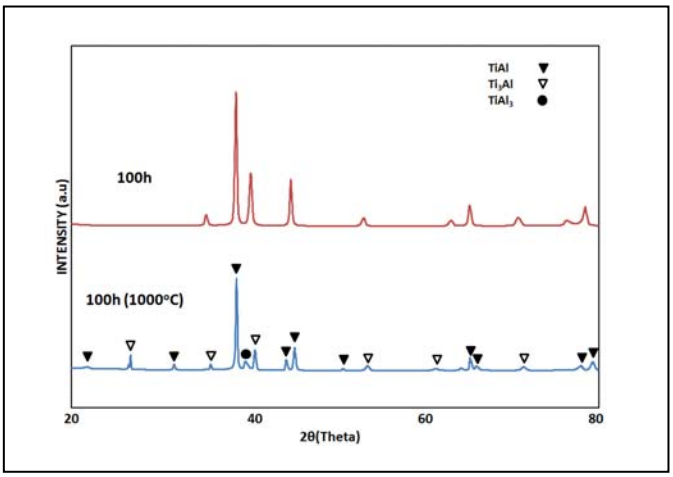

Fig. 6: X-ray spectrum of 100h milled Ti50%Al powders before and after heat treatment.

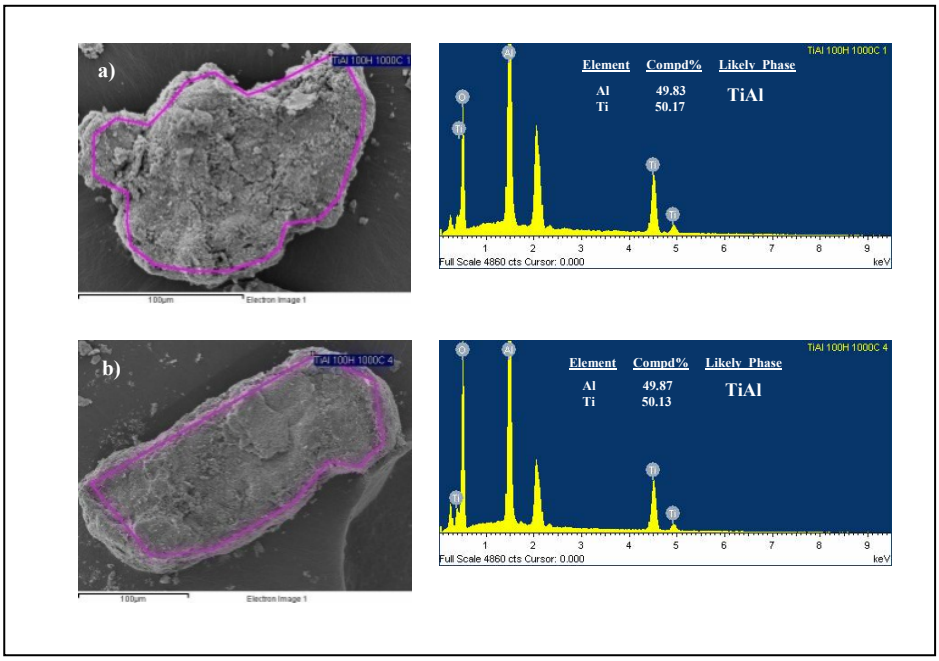

Fig. 7: FESEM image and EDX spectrum of Ti50%Al powder at 100h of milling duration with TiAl phase.

The investigation on the crystallite size after the heat treatment indicates that grain growth occurs after 40h of milling. Generally, the initial powder exhibits a gradual decreased in crystallite size up to 20h powder, but after 40h of mechanical alloying process, the crystallite size has increased gradually up to 80h powder. Eventually, the crystallite of 100h shows a decreased pattern but somehow the crystallite size of 34.7 nm is bigger compared to unheated powder of 21 nm. The grain growth of the Ti-50%Al powders were caused by a progressive recrystallization of powder particles, which is may due to its deformed morphology. Since, the powder precursor has already contained considerable amount of Ti(Al) solid solution by mechanical alloying alone, controlled heating up to 1000^0C for 2 hours, has resulted in the formation of different Ti-Al phases as discussed previously. This is well explained the various size of crystallite as the pre-alloyed powder has transform into multiple phases consist of γ-TiAl, α2-Ti_3Al, $TiAl_3$, AlTi and Al_2Ti after the heat treatment. As shown in Fig.8, the crystallite size of heat treated Ti-50%Al powders are varies with a minimum size at 32.15 nm for 20h milled powder, and maximum size at 80h mechanical alloyed powder at 57.8 nm.

4. Conclusions

The behaviours of of Ti50%Al powder mixtures during mechanical alloying have been investigated in terms of phase formation, microstructure and morphological changes throughout the process and after subsequent heat treatment, and the following conclusions can be drawn:

(i) Mechanical alloying of elemental Ti and Al powder mixture is an effective mean to synthesized a nanocrystalline Ti(Al) supersaturated solutions which exhibits a formation of TiAl phase after 40h of milling.

(ii) Subsequent heat treatment of powder milled for 80h exhibits the formation of a mixture of mainly α2-Ti_3Al plus γ-TiAl phases. On the other hand, 100h milled powder exhibits the formation of a major γ-TiAl with α2-Ti_3Al and a minor reflection of $TiAl_3$ phases.

(iii) Crystallite size refinement by MA shows a great reduction from 70nm of the initial powder mixture to 21nm after 100h of milling. On the other hand, the crystallite size of heat treated powder are varies and exhibits a grain growth after 40h of mechanical alloying process as a result of multiphases formation.

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