Synthesis and Characterization of Nano Ti-50%Al by Mechanical Alloying

Jinan B. Al-Dabbagh[1,C], **Rozman Mohd Tahar**[1], **Mahadzir Ishak**[2] **and Siti Aisyah Harun**[1]

[1] *Faculty of Industrial Sciences and Technology, University Malaysia Pahang, 23600 Gambang, Kuantan, Malaysia.*
[2] *Faculty of Mechanical Engineering, University Malaysia Pahang, 26600 Pekan, Malaysia.*
[C] **E-mail**: jdabbagh@ump.edu.my; **Tel:** +609-549 2767; **Fax:** +609-549 2766

1. Abstract

In this study, powder metallurgy process of TiAl nano alloys were performed via mechanical alloying (MA) of Ti-50%Al powder using planetary ball milling equipment. The characteristics of the powder samples including the compositions and microstructure changes were investigated by using X-ray diffraction and field emission scanning electron microscopy (FESEM) coupled with Energy-dispersive X-ray spectroscopy (EDX). Estimation by using Scherrer equation indicated that MA performed at different duration up to 15 have successfully refine the crystallite size from 89.51nm of Al to 28.29nm, and 67.6nm of Ti down to minimum of 17.17nm. Longer MA duration also exhibits a better effect on the thermal behaviour of Ti50%Al powders and micro-hardness value with gradual increased along with MA duration.

Keywords: TiAl alloys, mechanical alloying, nanostructured materials, thermal properties

2. Introduction

Over the past decades, intermetallic titanium aluminides particularly γ-TiAl based alloys, have gained a great deal of attention in numerous structural, non-structural and functional applications in different engineering fields [1-2]. Equipped with low density, high specific strength to weight ratio, good oxidation and corrosion resistance at elevated temperature [3-4], γ-TiAl based alloys are considered as a very promising material for potential replacement of Nickel base super-alloy and conventional titanium alloys in a high-temperature structure applications especially in aerospace, automotive and power turbine market [5-6]. However, the development and the actual utilization γ -based TiAl for structural applications are plagued by poor ductility and fracture toughness at room temperature [7-8]. The ductility of the γ -based TiAl alloy is very sensitive to microstructures. For example, the duplex (α2/γ) structure is significantly more ductile at room temperature, compared to lamellar or single equaxed γ structure [9].

New age strategies in the development of novel class material were by controlling of the microstructure to achieve a set of desired properties [10]. Advancement in micro alloying, composition modification, grain refinement to nanometer size and refining near-gamma grains and the lamellar colonies through heat treatment is a viable method to improve ductility as well as mechanical strength. One of the most promising methods to synthesize materials which can produce ultrafine, homogenous and manipulable microstructures is by mechanical alloying [11-12]. Hence, the production of an ultrafine and homogenous powder is predicted to overcome the scattering in mechanical properties due to the segregation in the composition of TiAl alloys in conventional manufactured by casting routes [13].

The purpose of this work is to synthesize and evaluate the formation of Ti-Al nano alloys compounds during MA process of elemental Ti and Al powders. The effect of subsequent heat treatment to powder processed up to 15h was also been studied. In addition, the thermal and mechanical properties of alloys product were investigated to .

3. Experimental

The MA processes were carried out using Retsch PM 100 planetary ball mill for duration varying from 5 to 15 h. Elemental powders of Ti (99.5%)-100 mesh and Al (99.97%) were mixed together to form a composition of Ti50Al50 (at.%). For each experiment, 5g of the powder mixture were poured into a tungsten carbide (WC) jar (250 ml). Tungsten carbide balls (ø10 mm) were used as a milling media with the ball-to-powder weight ratio is approximately up to 20:1. Small amount of Hexane was added as process control agent (PCA) to prevent excessive agglomeration of the powders to the milling tools. The jar then was air tight sealed and back-filled with pure Argon (99.9%) where the pressure in the jar was kept at 0.1 MPa. The rotation speed is set at 300 rpm with interval time at every 5 minutes. The milling was interrupted at selected 5h, 8h, 10h, 12h and 15h and a small amount of powder was removed for characterizations.

The MA process parameters and conditions as shown in Table 1 below;

***Table. 1**: MA parameters and conditions for Ti50%Al powders.*

Parameters	Conditions
Milling Type	Planetary ball mill (Retsch PM 100)
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	Up to 300 rpm
Milling duration	Up to 15 hours
Ball-to-powder mass ratio	Up to 20:1
Process control agent	Hexane
Environment	Ar (99.9% purity)

The Ti50%Al powders samples were mechanically alloyed under different parameters and conditions as in Table 2.

***Table.2**: MA group for Ti50%Al powders.*

Group		Rotation Energy	PCA's	Ball to Powder Mass Ratio
A	-	200rpm	nil	10:1
B	-	300rpm	Hexane (50%wt)	10:1
C	-	400rpm	Hexane (50%wt)	10:1
D	-	300rpm	Hexane (50%wt)	20:1
E	-	300rpm	Hexane (25%wt)	20:1

The surface morphology and microstructure of the processed powder were characterized by using a Zeiss Evo 50 scanning electron microscopy (SEM) at an accelerating voltage of 10 kV. X-ray measurements were applied to the samples to identify the powder component, phase transformation and structural changes of their crystal structure with a Rigaku Minitron X-ray diffractometer, using Cu Kα radiation (λ=1.54062 A°). Step-scanning has been carried out from 20 to 80Θ with a counting time of 5s every 0.02Θ. The crystallite size of the milled

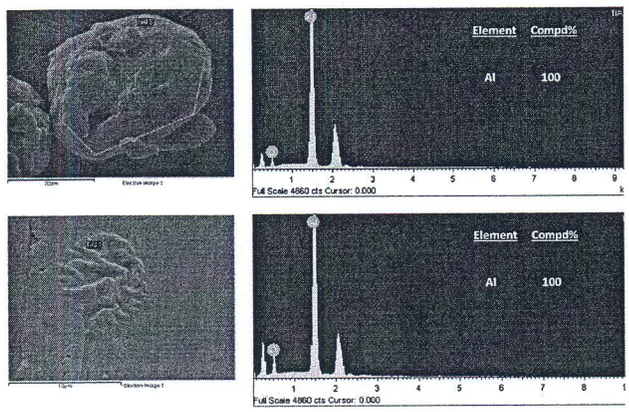

Figure 1. *FESEM images and EDX spectrums of unreact powder particles of B samples after 8h of milling.*

In contrast, even after 15h of milling, the XRD results only shows a gradual intensity decreased and peak broadening (Figure 2, 3, 4 and 5) . The crystallite size refinements were also slower and less progressive compared to A group. For instance, the B group (300rpm, 10:1 bpr, 50wt% Hexane) exhibits a crystallite size decreased of Ti to only 57.20nm, and Al to only 62.24nm after 6h of milling. Even after prolonged milling up to 15 h, the size only decreased to 56.58nm of Ti and 56.03nm of Al respectively. Whereas for C samples which were mechanically alloyed under higher rotation speed (400rpm, 10:1 bpr, 50wt% Hexane), the crystallite size reduction was slightly better as it was decreased to 49.85nm for Ti, and 55.61nm for Al after 6h. This is occurred as by increasing the rotation speed, the likelihood of collision between the ball to the powder and the milling jar has also increased.

The use of 20:1 ball to powder ratio in D group (300rpm, 20:1 bpr, 50wt% Hexane), somehow exhibits a better refinement of crystallite size compared to B group, as after 15h of milling, it was decreased to 44.95nm for Ti and 48.25nm of Al respectively. This result has also suggested that increased of the ball to powder weight ratio, has accelerated the MA process as the surface area for ball to powder impact has doubled. In the case of E group(300rpm, 20:1 bpr, 25wt% Hexane), which mechanically alloyed by using less amount of PCA for 15 h, more progressive refinement were observed as the Ti crystallite size was decreased to 42.28nm whilst Al was reduced to 50.41nm. The result obtained shows that, the amount of Hexane used during milling has also played an important role in grain refinement. In addition, all above results has also confirmed that the use of Hexane has delayed the alloying process as partial of the kinetic energy during milling were absorbed by PCA instead of the powder particles.

The nature of crystallite size reduction in MA is by the continuous cold welding, fracturing, re-welding and refracturing, resulting in the breaking of the powder particles and therefore the grain boundaries of the materials. In general, fracturing of ductile materials was not easy and it was difficult to obtain a very small crystallite size. As predicted, the Ti with less ductility (hcp structure) has a smaller size than that of very ductile Al (fcc structure) in the final powder product. These phenomena may occur due to crystallite size of the initial powder feed with 89.51nm of Al and 67.6nm of Ti. But the decreased rate of Ti crystallite size was much slower than Al, which in good agreement with the ductile-brittle material behaviour.

The observation of variation in crystallite size of Ti and Al in Ti50%Al powder samples, shows that the structure of the powder were strongly dependent on the mechanical alloying process conditions and parameters. It can be deduced from the result obtained; dry milling without an addition of PCA's is proved to be the most effective means in reducing the Ti50%Al crystallite size, despite the fact that, milling with higher rotation speed, higher ball to powder ratio and addition of less PCA resulted in better crystallite refinement.

Table 3. *Crystallite Size Evolution of Ti at various milling duration*

Milling Duration (h)	Crystallite size (nm)				
	A	B	C	D	E
0			67.6		
2	22.55				
4	17.17	59.12	59.89		
5					48.41
6	18.56	57.20	49.85		
8		58.70		68.36	
10		65.61		44.91	69.3
12		58.13		57.97	
15		56.58		44.95	42.48

Table 4. *Crystallite Size Evolution of Al at various milling duration*

Milling Duration (h)	Crystallite size (nm)				
	A	B	C	D	E
0			89.51		
2	40.33				
4	38.85	60.35	69.27		
5					53.39
6	28.29	62.24	55.61		
8		60.91		57.30	
10		57.10		48.92	62.68
12		62.31		48.74	
15		56.03		48.25	50.41

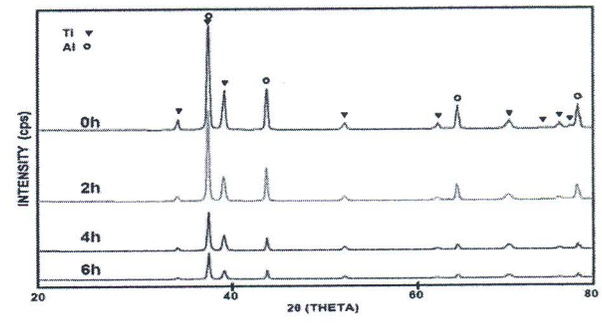

Figure 3. *X-ray diffraction spectrum of A group (Dry, 200rpm, 10:1) at various milling duration.*

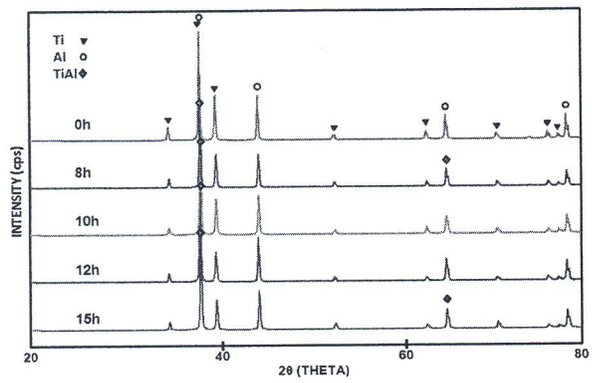

Figure 4. X-ray diffraction spectrum of B group (Wet 50wt% Hexane, 300rpm, 10:1) at various milling duration.

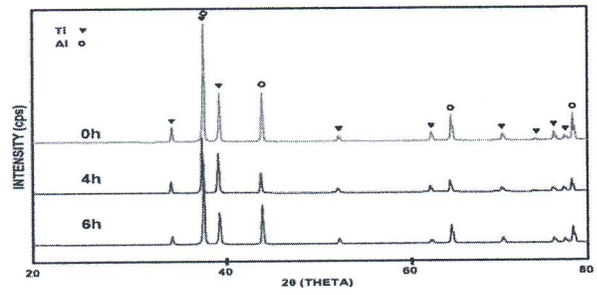

Figure 5. X-ray diffraction spectrum of C group (Wet 50wt% Hexane, 400rpm, 10:1) at various milling duration.

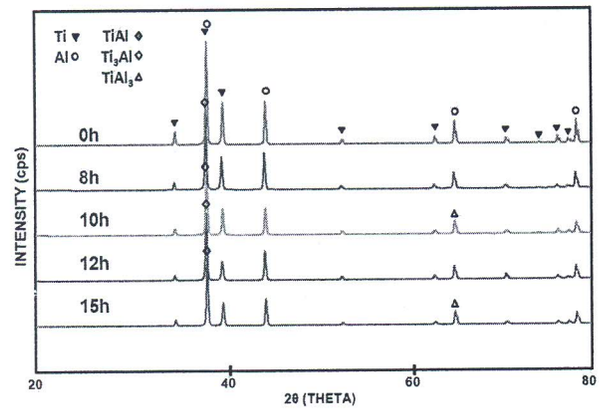

Figure 6. X-ray diffraction spectrum of D group (Wet 50wt% Hexane, 300rpm, 20:1) at various milling duration.

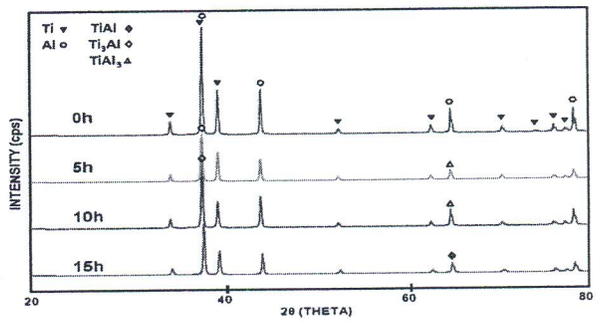

Figure 7. X-ray diffraction spectrum of A group (Wet 25wt% Hexane, 300rpm, 20:1) at various milling duration.

4.3 *Thermal stability of Ti50%Al powder*

Thermal analysis was performed by heating the powder sample in an alumina adapter in dynamic vacuum atmosphere up to 850°C at a heating rate of 10°C/min. As observed from the DTA spectrums of selected B samples, gas release occurs between 70–315°C temperature ranges. All spectrums also shows that the DTA peak appeared between 665-740°C. The minimum onset temperature for this sample was at 681.2°C for 8h MA-ed powder which corresponds to the melting of the Al phase, and maximum temperature of 689.50°C for 10h MA-end powder (Fig.16). Maximum point of exothermic peak were observed to appear within the temperature range of 697.9-702.8°C and between 56.3-65.743μV. This associate with the transformation of the metastable solid solution into the equilibrium TiAl phase. Accordingly, the maximum, onset, offset and reaction point of all samples increased gradually by milling duration over initial powder value as seen in Table.3.

The increased mechanochemical reaction temperature reflects a progressive intermixing or formation of nanocrystallite Ti(Al) solid solution as well as crystallite size refinement. As only single TiAl phase appear to form in these sample group, it is suggested that the reduction in crystallite size was the main reason in the shifting of DTA peak to a higher temperature. On the other hand, it is revealed that progressive intermixing and multiphase nanocrystallite Ti(Al) solid solution formation in D and E samples, has resulted in the shifting of exothermic peaks to even higher temperatures compared to B samples. As shown in Fig. 17, the DTA traces exhibit a better thermal properties as DTA peak for both samples appear to co-exist in the higher temperature range of 670-795°C with minimum onset temperature at 696.3°C for 15h(E) MA-ed powder and maximum temperature of 709.50°C for 12h(D) MA-ed powder.

Maximum points of exothermic peak were observed to appear within 713.1-726.1°C temperature range and between 163.6-171.4μV. As multiple TiAl phases appear to form in these sample group, it is well explained the inconsistency in DTA peak value. Whereas the increasing of heat changes suggested the energy consumed to induce the mechanochemical reaction is caused by the formation of nanocrystallite Ti(Al) solid solution as well as crystallite size refinement. This DTA observation further confirmed that the use of higher ball to powder ratio from 10:1 to 20:1 has accelerates the MA process as its resulting in better thermal behaviour.

powders was determined from X-ray line broadening by using the Scherrer equation;

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

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.

To study the thermal properties of the Ti-50%Al powders as well as the transformation of the powder products during heating, the samples were heated in dynamic vacuum atmosphere up to 850°C at a rate of 10°C/min in a Linseis P75 Platinum Series dilatometer. The results obtained including the value of differential thermal analysis (DTA) and coefficient of thermal expansion (CTE) analysis using Al_2O_3 as reference material. The powder then analyzed with XRD again to investigated the

Hardness tests were performed using a Matsuzawa MMT-X7 micro hardness test machine according to ASTM E 384-99 Standard Method under a load of 0.02 kg (VH20) for 10s. Prior indentation, Ti-50%Al powders were made into ø12mm pellet by pressed in a special mould at 100Psi for 10s, hot mounted in a polyester resin, cured for 8 days, polished and dried following powder metallurgical processing method.

4. Result and Discussion

4.1 *Morphological evolution of Ti50%Al powder*

The morphology of the MA-ed powder at different milling duration was investigated by SEM. For initial Ti50%Al powder mixture (0h), Ti particles appears in irregular shapes and various sizes as the initial Ti powder was in 100 mesh size, but Al particles are mainly in much smaller size with irregular shaped. In the initial stages 2h of MA, with the absences of PCA (A samples), it is appeared that the powder particles underwent a repeated cold welding, fracturing and re-welding resulting in the formation of rounded shaped beads and deformed particles Fig.1(b). Severe agglomeration of the powder to the balls and milling jar were observed due to ductility of Al. After 4h of milling, these beads and particles then evolved and disintegrate to dull and more uniform flake shaped particles. On further milling to 6h, As MA processed has increased the number of particles fracturing and refining, these flaky particles disintegrate more as uniform smaller size flakes and particles. But the major drawback of dry milling was severe sticking of the powder to the balls and milling jar during the process due to ductility of Al which were hard to be removed.

On the other hand, with an addition of Hexane as a process control agent in B, C, D & E group, the sticking of the powder to milling tool appeared to be very minimum and the formation of beads were not observed. The used of Hexane has proved to be an effective means to minimize agglomeration and to optimize the milling yield as the amount of agglomerated powder to the balls and milling jar were almost negligible. Only small size flaky particles were observed in the initial stages 2-4h. Further milling up to 8h, leads by increased deformation and work hardening, these flakes then turn into a finer and relatively smaller and by 15h, equiaxed particles with a homogeneous structure were obtained. The FESEM images of B samples after 8h of milling are shown in Figure 1.

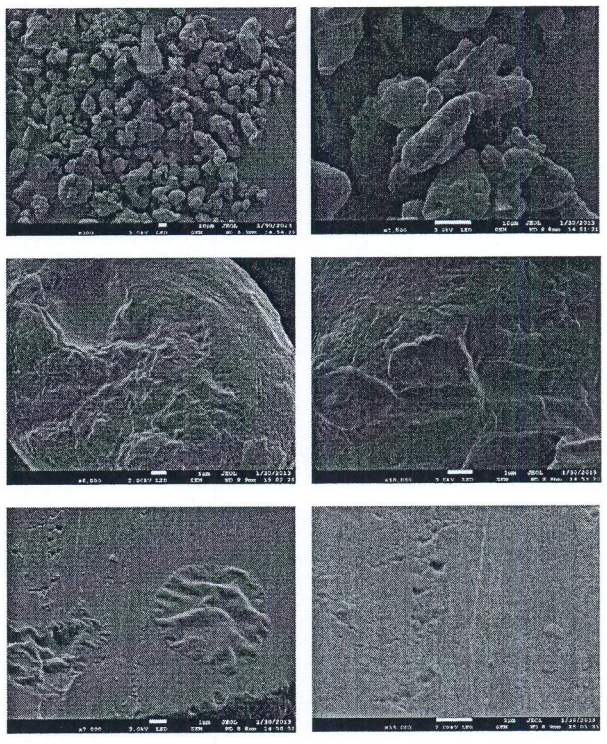

Figure 1. *FESEM images of B samples after 8h of milling. (a) and (b) powder particles, (c) and (d) particles morphology, (e) and (f) particle surface.*

4.2 *Crystallite size evolution of Ti50%Al powder*

The investigation of the Ti50%Al powders transformations for different milling duration up to 15h was followed by XRD. The XRD pattern of all sample groups exhibits the reflections of a well defined Ti and Al spectrums. In general, the Ti and Al peaks are weakened and broadened with increased in milling time to form a solid solution. The 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. The evolution in crystallite size of Ti and Al for respective samples group are calculated and listed in Table 3 and Table 4.

Amongst of all the sample, A group which was dry milled (200rpm, 10:1 bpr), exhibits a sharp intensity decreased and peak broadening (Figure 1) were observed due to the great decrease in crystallite size from 67.6nm of Ti and 89.51nm of Al in the initial Ti50%Al powder mixture to 18.76nm and 28.29nm respectively. Even though the result of this group shows a progressive decreased in crystallite size and disappearance of Ti and Al spectrums, it do not exhibit any new peaks neither intermetallic nor other compound. This result was in a good agreement of EDX analysis which identified some unreact particles as shown in Figure 2.

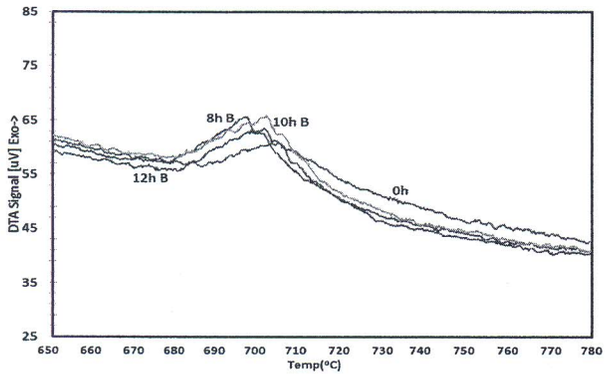

Figure 8. DTA thermogram for Ti50%Al powders B group at various milling duration up to 15h.

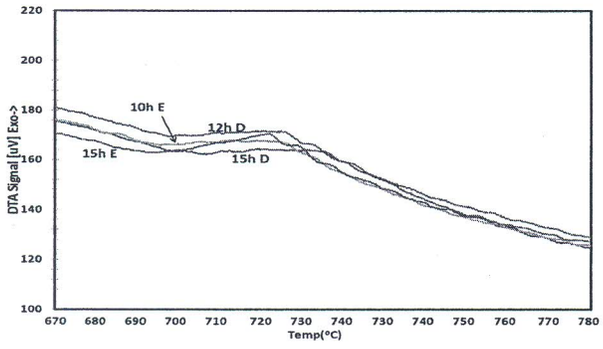

Figure 9. DTA thermogram for selected Ti50%Al powders D and E group at various milling duration.

***Table 5.**. DTA peak measurement data for selected Ti50%Al powder at various milling duration.*

SAMPLES	MILLING DURATION	ON SET	OFF SET	POINT OF REACTION	HEAT CHANGES
		TEMP (°C)			µVS
Initial	0h	675.80	697.10	678.50	1369.22
B	8h	681.20	704.40	685.70	1983.40
B	10h	689.50	708.80	696.80	2142.01
B	12h	687.00	711.70	691.60	2305.43
D	12h	709.50	739.90	719.80	2147.09
D	15h	708.70	750.20	717.40	2437.96
E	10h	698.4	739.1	701.7	2125.285
E	15h	696.3	738.3	702.1	2463.848

As shown in Fig.18 and Fig.19, it was found that the pattern of α-alpha (CTE) under controlled heating up to 850°C exhibits two different groups of spectrums as DTA result. B samples which milled with 10:1 ratio, exhibit a higher peak in a narrow peak range with CTE value range between 9.4357 – 10.9467 E-6/K, while D and E samples which milled with 20:1 ratio have a lower peak but wider peak range and lower CTE value range between 6.8785 – 9.7642 E-6/K.

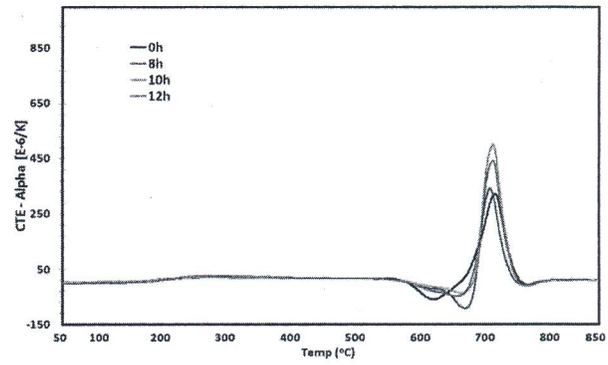

Figure 10. CTE thermogram of selected Ti50%Al powders at various milling duration of B group..

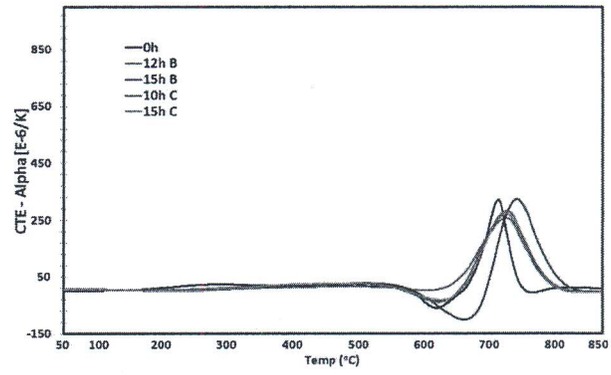

Figure 11. CTE thermogram of selected Ti50%Al powders at various milling duration of D & E group.

4.5 Micro-hardness of Ti50%Al Powder

Micro-hardness test were performed on selected samples at various milling duration. The test result for each sample is the average value of at least 10 successive indentations. As shown in Fig.20, the micro hardness values of D samples have gradually increased over milling duration. After 12h of MA, the micro hardness value is 2 times higher than the initial powder mixture (0h). The increased of Ti50%Al hardness is not only due to increased fineness of the Ti-Al powder microstructure but also due to the formation of formation Ti(Al) solid solutions or both.

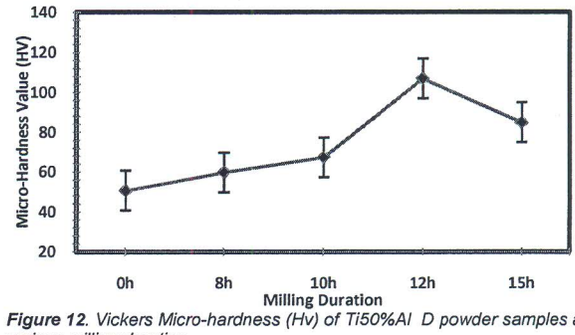

Figure 12. Vickers Micro-hardness (Hv) of Ti50%Al D powder samples at various milling duration.

5. Conclusion

The results of this study show that milling parameter plays an important role in the efficiencies of MA process;

i. Mechanical alloying (MA) of elemental Ti and Al powders has promotes the formation TiAl alloys. Longer milling duration and less addition of hexane resulted in a better formation of TiAl alloys as Ti(Al) solid solution was formed after 5h of milling.

ii. Dry milling without an addition of PCA's led to a dramatic decrease in the crystallite size of powder product but the agglomeration effect resulted in low milling yield. In contrast, with an addition of hexane, even though effectively minimize the agglomeration problem, proved to delay the MA process.

iii. Higher rotation energy, less addition of PCA and higher ball to powder weight ratio could accelerate the crystallite size reduction.

iv. Longer milling duration exhibits a better effect on the thermal behavior of Ti50%Al powders as the reaction temperature has increased to 719.80°C compared with 678.50°C of initial powder mixture. As in the DTA results, the observation on α-alpha value shows that bigger ball to powder weight ratio used in MA were also resulted in better thermal behavior.

v. The micro-hardness value of the MA-ed powders systematically increased by milling duration with maximum value of 106.93 Hv for 12h MA-ed powder as a result of grain refinement and the formation new phases.

It can be conclude that the physical and thermal behaviour of Ti50%Al powder in the early stage of MA, were determined by the morphology and microstructure of powder samples. By further MA in the intermediate and final stage, progressive intermixing between the Ti-Al plays a vital role in determining the changes in the physical and thermal behaviour.

6. Acknowledgement

This work was supported by UMP Research Grant under research project UMP RDU 100370.

7. References

[1] Bhattacharya P, Bellon P, Averback RS, Hales S. Nanocrystalline TiAl Powders Syntehsized By High-Energy Ball Milling: Effects Of Milling Para-Meters On Yield And Contamination. Journal Of Alloys And Compounds 368 (2004):187–96.

[2] N. Forouzanmehr, F. Karimzadeh, M.H. Enayati, Study On Solid-State Reactions Of Nanocrystalline TiAl Synthesized By Mechanical Alloying, Journal Of Alloys And Compounds 471 (2009):93–97

[3] M. Goral, L. Swadzba, G. Moskal, G. Jarczyk, J. Aguilar, Diffusion aluminide coatings for TiAl intermetallic turbine blades, Intermetallics 19 (2011):744-747

[4] M. Yamaguchi, H. Inui And K. Ito, High-Temperature Structural Intermetallics, Acta Materialia. 48 (2000):307-322

[5] Kunal Kothari, Ramachandran Radhakrishnan, Norman M. Wereley, Advances In Gamma Titanium Aluminides And Their Manufacturing Techniques, Progress In Aerospace Sciences(2012), http://Dx.Doi.Org/10.1016/J.Paerosci.2012.04.001

[6] GE-Aviation:Genx.GE.[Online],2007. http://www.Geae.Com/Engines/Commercial/Genx/S

[7] D. Hu, Effect of composition on grain refinement in TiAl-based alloys, Intermetallics 9 (2001):1037–1043.

[8] F. G. Cuevas, J. Cintas, J. M. Montes, J. M. Gallardo, Al–Ti Powder Produced Through Mechanical Alloying For Different Times, Journal Of Material Sciences 41 (2006):8339–8346

[9] FANG Wen-Bin, LI Xue-Wen, SUN Hong-Fei, DING Yong-Feng, Characterization Of Ti-50%Al Composite Powder Synthesized By High Energy Ball Milling, Trans. Non-Ferrous Met Soc. China 21 (2011):333-337

[10] Mohammad Reza Farhang, Ali Reza Kamali, Masoud Nazarian-Samani, Effects Of Mechanical Alloying On The Characteristics Of A Nanocrystalline Ti–50at.%Al During Hot Pressing Consolidation, Materials Science And Engineering B 168 (2010):136–141

[11] LI Xue-Wen, SUN Hong-Fei, FANG Wen-Bin, DING Yong-Feng, Structure And Morphology Of Ti-Al Composite Powders Treated By Mechanical Alloying, Trans. Non-Ferrous Met Soc. China 21(2011):338-341

[12] Brian Gabbitas, Peng Cao, Stella Raynova, Deliang Zhang, Microstructural Evolution During Mechanical Milling Of Ti/Al Powder Mixture And Production Of Intermetallic Tial Cathode Target, Journal Of Material Sciences 47(2012):1234–1243

[13] Fadeeva VI, Leonov AV, Szewczak E, Matyja H. Structural Defects And Thermal Stability Of Ti(Al) Solid Solution Obtained By Mechanical Alloying. Materials Science And Engineering A242 (1998):230–234.