Effect of the Milling Parameters on the Characteristics of Ti-50%Al Nanocrystallite Synthesized by Mechanical Alloying (MA)

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Abstract

Titanium aluminide nano alloys has been successfully produced by mechanical alloying (MA) technique in a planetary ball mill and followed by subsequent heating. The influence of milling parameters such as the milling duration, rotation speed and balls to powder mass ratio on the characteristics of the Ti50%Al powder including the micro structural, crystallite size refinement and the phase formation were investigated. It was found that mechanical alloying of elemental Ti and Al powders has promotes the formation of Ti(Al) solid solution with great crystallite size refinement. Subsequent heating up to 850^{o}C resulted in a formation of new intermetallic with a dominant $TiAl_3$ phase.

Keywords: Titanium aluminide, nanostructured materials, x-ray diffraction

1. Introduction

Titanium aluminide base-alloys hold a great potential as high performance materials especially as a high temperature structure in aerospace, automotive and land-based applications particularly in replacing Ni-base super-alloy where weight reduction is crucial. This material offers a great combination of an excellent corrosion resistant, low density at about 4.0 g/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 high temperatures [1-3]. Even though the development of TiAl based alloys has began since in the 70's, it is plagued by poor ductility at ambient temperature below 700^{o}C, low strength at elevated temperature, and insufficient oxidation resistance above 850^{o}C [2-4]. The commercialization of TiAl only started in 90's when TiAl turbocharger for F1 and sport cars make it first entrance in the market [4-5]. Recently, General Electric (GE) has started its commercialization of TiAl base alloy for its low-pressure turbine (LPT) blades in GEnx type engines that's powered Boeing's 787 Dreamliner passenger craft [5-6].

Crystallite refinement of the microstructures to nanometer size, composition modification, and refining near-gamma grains and the lamellar colonies through heat treatment is a viable method to improve ductility as well as mechanical strength [7-8]. One of the most promising methods to synthesize materials which can produce ultrafine, homogenous and manipulable microstructures and desired properties is by mechanical alloying [8-10]. But its complex process involves a large degree of uncertainty as it is very sensitive to experimental conditions such as type of milling equipment, milling duration, energy input, type and amount of process control agents (PCA) and atmosphere [11].

The purpose of this study is to investigate the effect of milling parameters on the micro structure, crystallite size refinement and phase formation of TiAl nano alloys synthesized via mechanical alloying and its relation on the mechanical properties.

2. Experimental

Commercial-grade elemental powders of Ti (99.5%)-100 mesh and Al (99.97%) from Acros Organics, New Jersey, U.S.A. were used as starting materials. Ti and Al powder were weighted on an electronic scale in a ceramic vial with an initial weight of 5g for each experiment. The MA process was carried out using a Retsch PM 100 planetary ball mill for different milling duration up to 15 hours. The powder mixture was poured into a tungsten carbide (WC) jar (250 ml) with tungsten carbide balls (10 mm ø) where the ball-to-powder weight ratio is approximately up to 20:1. Different amount of Hexane as PCA was added for selected samples. The jar then was back-filled with pure Argon (99.9%) where the pressure in the vial is kept at 0.1 MPa. The rotation speed is set up to 400 rpm with interval time at every 5 minutes. The milling was interrupted at selected times and a small amount of powder was removed for

characterizations and study. Table 1 shows the MA parameters and conditions employed throughout this research work. The MA processes were carried under five (5) different set of milling parameters as shown in and Table 2.

***Table. 1**: MA 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	200, 300 & 400 rpm
Milling duration	Up to 15 hours
Ball-to-powder mass ratio	10:1 & 20:1
Process control agent	Hexane (50%wt & 25%wt)
Environment	Ar (99.9% purity)

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

Set		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

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 the CuK_α (λ = 1.540562 A°) radiation. Step-scanning has been carried out from 20 to 80Θ with a counting time of 5s every 0.02Θ. The surface morphology and microstructure of the milled powder were characterized by using a Zeiss Evo 50 scanning electron microscopy (SEM) at an accelerating voltage of 10 kV. The Scherrer equation was used to estimate the crystallite size from broadening of XRD peaks;

$$D = \frac{0.9\lambda}{\beta \cos \Theta}$$

where $\beta = (\beta_M^2 - \beta_I^2)^{1/2}$, β_M is the full width at half maximum (FWHM) obtained, β_I is the correction factor for instrument broadening, Θ is the diffraction angles of the peak, λ is the CuK_α weighted wavelength (λ = 0.1540562 nm) of X-ray and D is the mean crystallite size.

Vickers micro hardness tests were performed using a Matsuzawa MMT-X7 micro hardness test machine according to ASTM E 384-$99^{\varepsilon 1}$ Standard Method under a load of 0.02 kg (VH20) for 10s.

3. Result and Discussion

3.1 Microstructure and Morphology

The surface morphology of the MA-ed powder at different milling duration was investigated by SEM. As shown in **Fig.1(a)**, for initial Ti50%Al powder mixture (0h), Ti particles appears in irregular shapes and various sizes and Al particles are mainly in much smaller size. In the initial stages of 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, as shown in **Fig.1(c)**. On further milling to 6h, as MA processed has increased the number of particles fractured and refined, these flaky particles disintegrate more to a uniform smaller size flakes and particles as shown in **Fig.1(d)** with finer and flattened surface. This phenomenon has also observed by several researchers [13-16]. As it was difficult to remove the agglomerated powder to milling balls and jar, dry milling was not continued further in this study.

On the other hand, with addition of 50%wt and 25%wt of Hexane as a process control agent (B, C, D & E samples) the agglomeration of the powder to milling tool appeared to minimized and the formation of beads were not observed. Only small size flaky particles were observed in the initial stages of 2-4h milling. Further milling up to 8h, leads to increase deformation and work hardening, these flakes then turn into a finer and relatively smaller and after 15h of milling, equiaxed particles with a homogeneous structure were obtained (not shown). 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.

For powder heated in a dynamic vacuum atmosphere up to 850°C, all samples had undergone a tremendous amount of grain growth. As shown in **Fig.2**, it is appeared that both samples have a crumble like surface, as heating had led to recrystallization.

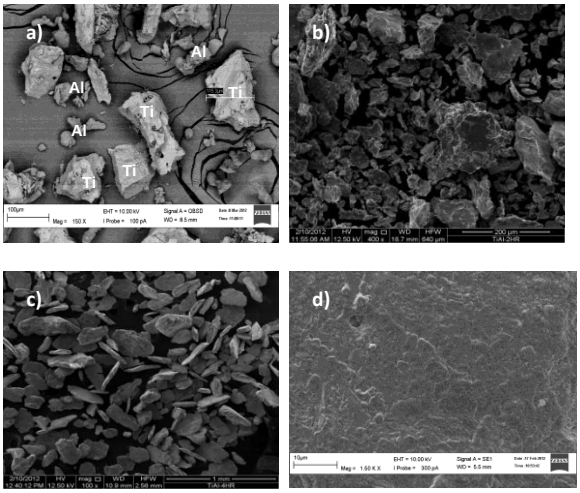


Figure 1. *SEM micrographs of Ti50%Al powders for different milling times. (a) Initial powder, (b) 2h MA-ed powder, (c) 4h MA-ed powder, and (d) surface morphology of 6h MA-ed powder particles.*

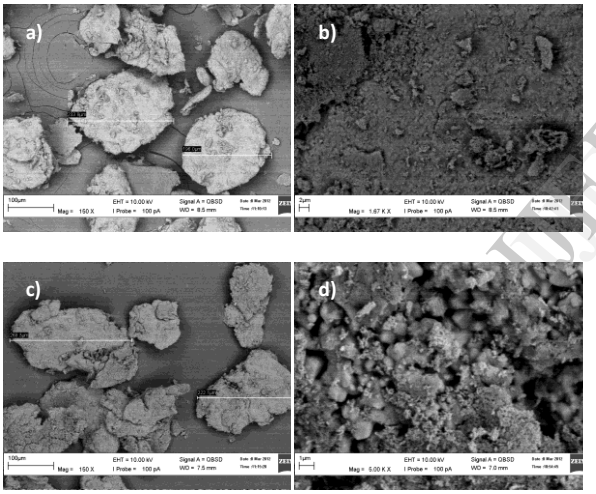


Figure 2. *SEM micrographs of Ti50%Al powders for different milling times after heating at 850^{o}C. (a) 4h MA-ed powder, (b) surface morphology of 4h MA-ed powder, (c) 6h MA-ed powder, and (d) surface morphology of 6h MA-ed powder.*

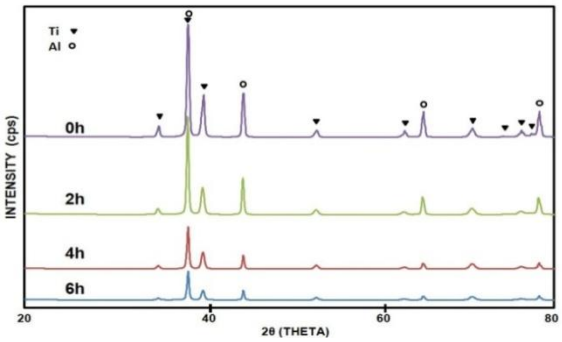
3.2 XRD Analysis

3.2.1 Characteristic of Ti50%Al MA-ed up to 6 hour (A, B & C Samples)

The investigation of the Ti50%Al powder transformations for different milling duration up to 6h was followed by XRD. All samples shows a polycrystalline structure of Ti(Al) solid solution (**Fig.3,4 & 5**). For powder MA-ed under 200rpm, without Hexane and 10:1 ball to powder weight ratio (samples A), sharp intensity decreasing and peak broadening were observed due to the great decrease in crystallite size from 42.61nm to about 20.7nm (**Fig. 3**). This size was calculated using the Scherrer equation from the XRD results.

In contrast, for B samples which were MA-ed under 300rpm, with 50%wt of Hexane, it was appeared that after 6h of milling, less progressive in intensity and peak broadening along with the crystallite size decreased to 38.72nm (**Fig.4**). Whereas for C samples which were MA-ed under higher rotation energy (400rpm), even though a significant peak broadening were observed, somehow exhibit an increasing in intensities from 4h to 6h. But the crystallite size reduction was slightly better than B samples as it was decreased to 36.02nm after 6h of milling as shown in **Fig.5**. The XRD pattern of all samples exhibit the reflections of the two elemental Ti and Al spectrums. Even though the result shows a progressive disappearance of Ti and Al peaks with milling time up to 6h, it do not exhibit any new peaks neither intermetallic nor other compound for all A, B, and C samples.

Fig.6 shows the relation between the crystallite size and milling duration under different parameters and conditions of MA. As a comparison, dry milling without an addition of PCA's proved to be the most effective means in reducing the crystallite size. These result has also confirmed that the use of Hexane has delayed the refinement process as partial of the kinetic energy during milling were absorbed by PCA. In addition, milling with higher rotation speed(rpm), were also leads to a better result in crystallite refinement as by increasing the rotation energy used it has increased the likelihood of impact between the ball



to the powder and the milling jar.

Figure 3*. X-ray diffraction for Ti50%Al MA-ed powders under 200rpm, 10:1, without Hexane (A Samples) up to 6h.*

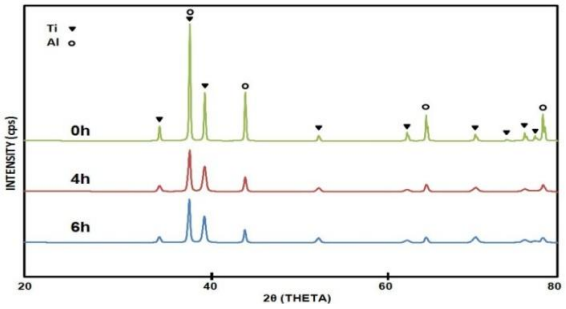


***Figure 4**. X-ray diffraction for Ti50%Al MA-ed powders under 300rpm, 10:1, with 50%wt of Hexane (B Samples) up to 6h.*

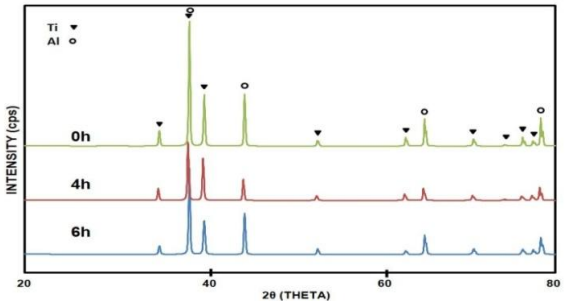


***Figure 5**. X-ray diffraction for Ti50%Al MA-ed powders under 400rpm, 10:1, 50%wt of Hexane (C Samples) up to 6h*

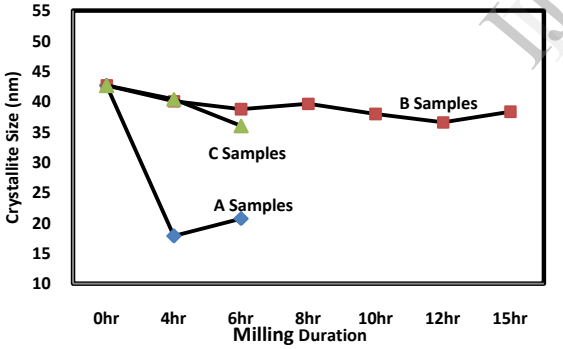


***Figure 6**. Comparison on average crystallite size of Ti50%Al MA-ed powders with and without Hexane at various milling times.*

3.2.2 Characteristic of Ti50%Al MA-ed up to 15h (B, D & E Samples)

The progressive development of crystallite reduction and the formation of solid solution Ti-Al phases for B, D & E samples which MA-ed up to 15h were examined by XRD. It was found that after 8h of milling, the peak intensity of B sample were increased gradually from 8h to 15h, with constant peak broadening compared to 6h MA-ed sample. Increased in peak intensity was also observed by Fadeeva [12] after 3h of milling, because the h.c.p. phase becomes the main phase in the alloy. Compared to the initial Ti50%Al powder, B sample shows a decreased in intensities and peak broadening, whereas the crystallite size was decreased to 38.3nm after 15h of milling. As shown in **Fig.7**, the XRD pattern also shows the shifting towards higher angles and overlapping of both Ti and Al peaks, along with the displacement of some Al peaks. This is related to the reduction of the lattice parameter, due to Al dissolution into Ti matrix which suggested the formation of nanocrystalline Ti(Al) solid solution as the appearance of TiAl phase on the principal peaks of all B samples were consistent from 8h-15h of milling.

Observation of ball to powder mass ratio effect shown that powder MA-ed with 20:1 ratio have a better effect on crystallite size refinement compared to 10:1 ratio. By increasing the ratio, the crystallite size after 15h of milling was reduced to 34.1nm for D samples as shown in **Fig.8**. It was also observed that intensities decreasing and peak broadening were more progressive compared to B samples, but the formation of nanocrystalline Ti(Al) solid solution is rather inconsistent and varies by milling duration from 8h-15h (**Fig.9**). For instance, powder MA-ed at 8h and 12h, exhibits only the appearance of Ti_3Al phase, while 10h MA-ed powder exhibits the formation of Ti_3Al and $TiAl_3$ phase, whereas for 15h MA-ed powder, TiAl and $TiAl_3$ were formed. This result suggested that the degree of intermixing between Ti and Al for this sample is higher than B samples. 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.

The amount of Hexane used during milling has played an important role in grain size refinement. After 15h, powder MA-ed with 25%wt Hexane has resulted in more progressive grain size refinement as it was reduced to 33.63nm for E samples as shown in **Fig.10**. As observed, the formation of nanocrystalline Ti(Al) solid solution was also inconsistent and varies, but it was found that its formation appear to be at earlier milling stage of 5h (**Fig.11**). This result has confirmed that the use of Hexane has delayed the MA process as partial of the kinetic energy were absorbed by PCA instead of the powder particles. For powder MA-ed at 5h and 10h in this group of samples, $TiAl_3$ and $TiAl_3$ phase were observed, while the 15h MA-ed powder exhibits the formation of TiAl phase.

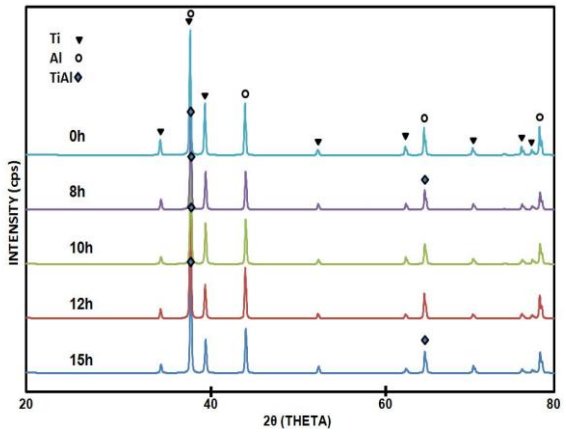


Figure 7. *X-ray diffraction for Ti50%Al powders MA-ed under 300rpm, 10:1, 50%wt of Hexane (B Samples) up to 15h.*

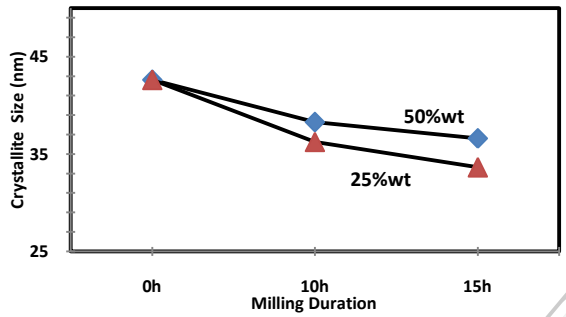


Figure 8. *Comparison on average crystallite size of Ti50%Al powders milled with different amount of Hexane at various milling times. (D vs E).*

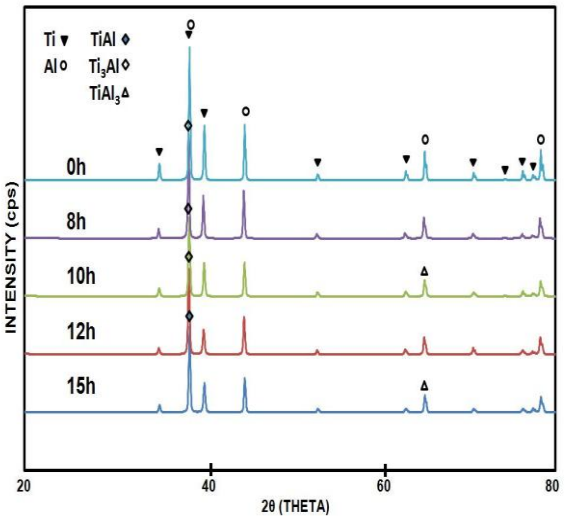


Figure 9. *X-ray diffraction for Ti50%Al powders MA-ed under 300rpm, 20:1, 50%wt of Hexane (D Samples) up to 15h.*

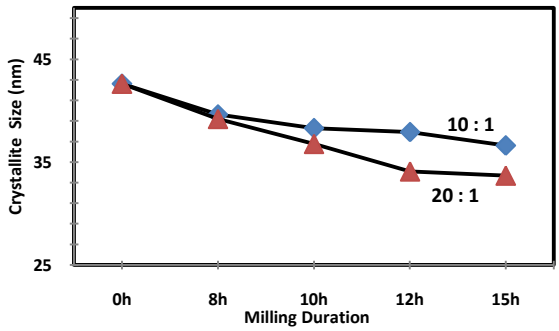


Figure 10. *Comparison on average crystallite size of Ti50%Al powders milled with different ball to powder ratio (B : P) at various milling time (B vs D)*

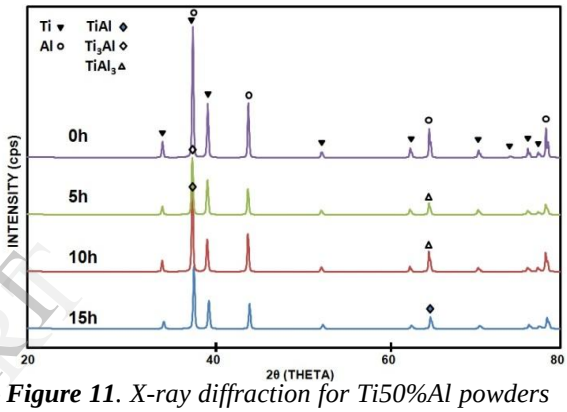


Figure 11. *X-ray diffraction for Ti50%Al powders MA-ed under 300rpm, 20:1, 25%wt of Hexane at various milling times (E Samples).*

3.2.3 Characteristics of Ti50%Al Powders After Subsequent Heating at 850°C

XRD patterns of MA-ed powder after control heating under vacuum 10^{-2} Torr condition up to 850°C exhibits a major difference from unheated one. In the case of A sample, the powder becomes almost entirely single-phase, with the formation of a dominant $TiAl_3$ phase plus a minor γ-TiAl phase as shown in **Fig.12**. The powder also exhibits an increased in crystallite size to 37.15nm for 6h MA-ed powder which probably caused by its coarse particle size and deformed morphology of powder particles. For C samples, it was observed that after the exothermic reaction in the thermal process, a mixture of $TiAl_3$ and α2-Ti_3Al phase were formed for 4h MA-ed powder, and as for 6h-MA-ed powder, a dominant of $TiAl_3$ along with a minor γ-TiAl phase was presents. Whereas for E sample, a single phase of $TiAl_3$ were formed for both 10h and 15h samples. From this result, it was found that longer milling duration up to 10h resulted in the formation of an entirely single-phase $TiAl_3$ after controlled heating at 10°C/min up to 850°C in a vacuum atmosphere. The result also

shows a significant decreased in crystallite size down to 31.31nm for 15h MA-ed powder.

Similar formation of a dominant $TiAl_3$ phase plus a minor γ-TiAl phase was also observed in B samples up to 10h MA-ed powder. But the result after 12h of MA-ed of B samples were rather complicated as a formation of entirely single-phase $TiAl_3$ was observed and a dominant $TiAl_3$ phase along with α2-Ti_3Al were formed after 15h of MA-ed (Fig.12). In contrast, all these powders up to 15h MA-ed exhibits a significant decreased in crystallite size with minimum 27.45nm for 12h MA-ed powder as shown in **Fig.13**. The formation of multiple phases of TiAl was also found by Gabbitas [13], after samples being heated at 1000°C. This result suggested that heating has transformed the Ti-Al powder mixture into TiAl intermetallics due to the phase transition of the metastable Ti (Al) solid solution into equilibrium TiAl intermetallic phase.

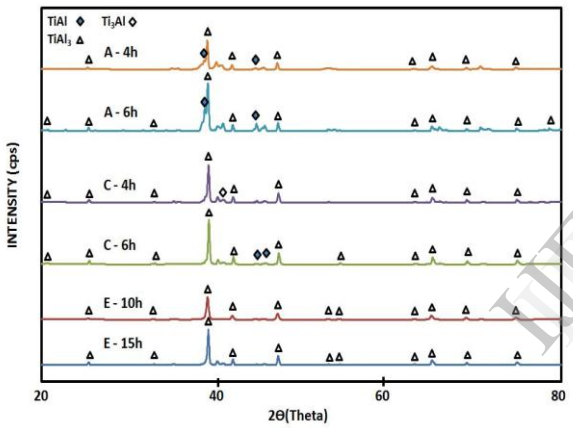


***Figure 12**. X-ray diffraction for Ti50%Al powders after heating up to 850°C of A, C & E samples.*

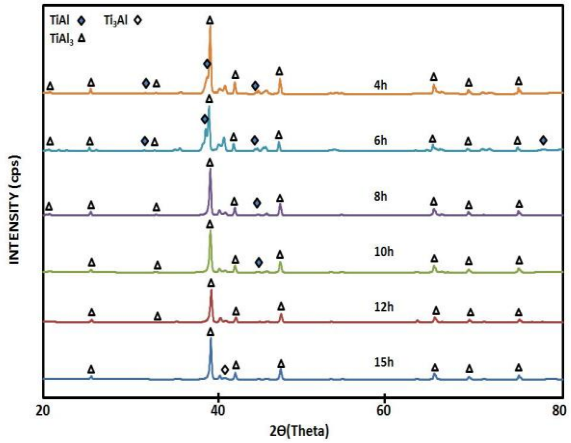


***Figure 13**. X-ray diffraction for Ti50%Al powders after heating up to 850°C of B samples.*

3.3 Micro-hardness Measurement

Micro-hardness test were performed on selected pressed 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.14**, MA produces a rapid, almost linear increase in micro-hardness over that of the initial mixture of Ti50%Al powder by 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 new phase of Ti-Al alloys or both. In this case, the gradual increase of hardness up to 12h samples is probably due to the decreased of crystallite size by milling duration. But the decrease of hardness at 15h powder is suggested cause by the formation of dual phase TiAl and $TiAl_3$ which have lower energy compared to single phase Ti_3Al in 12h powder.

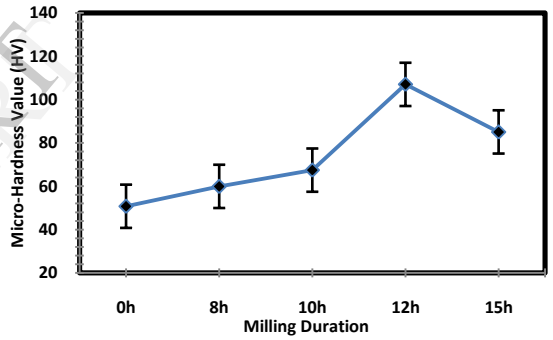


***Figure 14**. Vickers Micro-hardness (Hv) of Ti50%Al D powder samples at various milling duration.*

4. Conclusion

The results of this study show that milling parameter plays an important role in the efficiencies of mechanical alloying (MA) of elemental Ti and Al powders.Dry milling without an addition of PCA's led to a dramatic decrease in the crystallite size of powder product to 17.8nm after 2h of milling, 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 crystallite refinement process as the crystallite size was only reduced with a minimum value of 33.64nm. Whereas, higher rotation energy and higher ball to powder weight ratio could accelerate the MA process as milling at 400rpm and resulted in better crystallite size reduction.

Control heating up to 850^{o}C at a rate of 10^{o}C/min resulted in a significant reduction of crystallite size and the formation of new intermetallic phase with a dominant $TiAl_3$ phase plus minor γ-TiAl or α2-Ti_3Al phase or both. 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 crystallite size refinement and the formation new phases.

5. References

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