

# THE INFLUENCE OF PROCESS CONTROL AGENT (P.C.A)'S STATE ON EXPEDITION OF MECHANICAL ALLOYING OF NANOSTRUCTURE TiAl( $\gamma$ ) ALLOY

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**Abstract** In this research, the effect of two process control agent: methanol (liquid state) and stearic acid (solid state) on mechanical alloying process of Ti and Al with equal at%(Ti<sub>50</sub>Al<sub>50</sub>) were investigated. Phase transformation at presence of two PCA was: at first, powder mixture was transformed to a metastable solid solution of Al in Ti lattice (disordered hcp) and then transformed to amorphous phase with increasing the alloying time. The results showed that the state and type of PCA is effective in expedition of mechanical alloying process. The metastable solid solution phase (dis. hcp) at presence of methanol was achieved more quickly than stearic acid was used. Changes in grain size, lattice strain, weight recovered and impurity content of milling parameters at presence of two different PCA were studied. At last with annealed of last product of alloying, the TiAl( $\gamma$ ) phase with high purity and nanostructured form were produced.

**Keywords** Titanium Aluminide, Mechanical Alloying, Nanostructure, Process Control Agent

**چکیده** در این تحقیق، اثر دو عامل کنترل کننده فرایند: متانول (حالت مایع) و اسید استئاریک (حالت جامد) بر روی فرایند آلیاژسازی مکانیکی مخلوط تیتانیوم و آلومینیوم با درصد اتمی برابر (Ti<sub>50</sub>Al<sub>50</sub>) مورد تحقیق قرار گرفت. استحاله فازی در حضور دو عامل کنترل کننده فرایند بدین گونه بود که در ابتدا، مخلوط پودری به محلول جامد نیمه پایدار آلومینیوم در تیتانیوم تبدیل و سپس با افزایش زمان آلیاژسازی به فاز آمورف تبدیل شد. نتایج نشان داد که حالت و نوع عامل کنترل کننده فرایند در تسریع فرایند آلیاژسازی مکانیکی موثر است. فاز نیمه پایدار محلول جامد در حضور متانول سریعتر از زمان حضور اسید استئاریک بدست آمد. تغییرات در اندازه دانه، کرنش شبکه، وزن قابل بازیابی و میزان ناخالصی در حضور دو عامل کنترل کننده فرایند به طور جداگانه مورد مطالعه قرار گرفت. نهایتاً با آنیل محصول نهایی آلیاژسازی، فاز TiAl( $\gamma$ ) با خلوص بالا و نانو ساختار تولید شد.

## 1. INTRODUCTION

Intermetallic compounds of the Ti-Al system and alloys based on these compounds such as TiAl( $\gamma$ ), Ti<sub>3</sub>Al( $\alpha$ ) are materials of rapidly growing technological importance. Such alloys have a combination of good high-temperature mechanical properties with good environmental resistance and low density and good oxidation/corrosion resistance [1-5]. The Ti-Al binary diagram is shown in Fig. 1.

This combination of useful properties makes them very attractive as high temperature structural

materials for aerospace, automotive and other application [5-7].

Mechanical alloying (MA) is a unique process for fabrication of several alloys and advanced materials at room temperature. MA is a process to prepare powders in which solid state reactions are caused to occur when materials are processed in a ball mill [7-9]. During high-energy ball milling the powder particles are repeatedly cold welded, fractured and rewelded between the balls and the vial of the milling. During MA heavy deformation is introduced into the particles. This is manifested by the presence of a variety of crystal defects such

as dislocations, vacancies, stacking faults and increased number of grain boundaries. The presence of this defect structure enhances the diffusivity of solute elements into matrix [9-11].

Conventional casting of TiAl-base intermetallics is difficult due to their relatively high melting temperature and the extreme reactivity of titanium. More importantly, however, cast TiAl alloys are usually not suitable for subsequent forming as a result of inhomogenities and segregation in the solidification microstructure combined with the lack of ductility [13].

In MA the cold welding and fracturing process enables powder particles to be always in contact with each other with atomically clean surfaces and with minimized diffusion distance. The essential condition for a successful mechanical alloying process is the balance between cold welding and fracturing. However, this balance in most cases may not be obtainable by the milling process itself [13-14]. In order to obtain the balance between fracturing and welding, PCA is normally used in the milling process. When ductile metals are milled the use of a PCA is necessary in order to avoid excessive cold welding that would lead to an increase in particle size and considerable sticking of the powders to the milling tools [13-15].

In mechanical alloying, PCA is added to powder mixture during milling to reduce the effect of cold welding. The PCA's can be solids, liquids or gases. PCA's are mostly organic compounds which adsorb on the metal surface and thereby impend

the clean metal-to-metal contact and minimizes cold welding between powder particles and thereby inhibits agglomeration. For example methanol, Ethanol, stearic acid and ... are some PCAs [14-16].

## 2. EXPERIMENTAL PROCEDURE

Titanium and Aluminum of more than 99.5% purity and particle size 100-150 $\mu$ m were used as a starting powders to reach Ti<sub>50</sub>Al<sub>50</sub>( $\gamma$ ). The powders weighted in a glove box with argon atmosphere. The FP4 planetary mill with two tempered steel vials with steel balls was employed in this research. The capacity of each vial was 250ml. The diameters of balls were 15, 20mm. The vials were designed to allow pumping and subsequent filling by an inert gas (Ar) with high purity (near to 100% purity). The final gas pressure in the vial was kept to be 0.1 Mpa. Two different PCA's that investigated in this study were methanol and stearic acid. The ball-to-powder weight ratio and speed of rotation of supporting disk were 15:1 and 450 rpm, respectively. The maximum alloying time accumulated was 50h. To avoid temperature increases, periods of 0.5h were alternated with an equal rest time. After alloying time (5, 10, 15, 20, 30, 50h), the powders were withdrawn from the vials for analysis (XRD).

XRD measurements were performed by Bruker-D8-Advanced, using Cu-K $\alpha$  radiation at 30kv and 20mA. Analysis of the powder morphology and particle size measurements was achieved by Cam Scan MV-2300 SEM with EDS analyzer at an accelerating voltage of 25Kv.

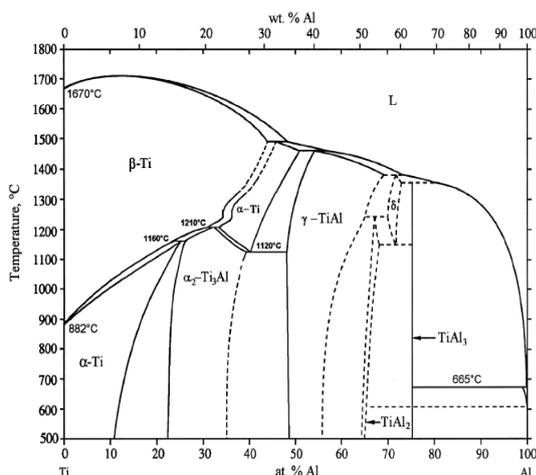


Figure 1. The Ti-Al Diagram [12].

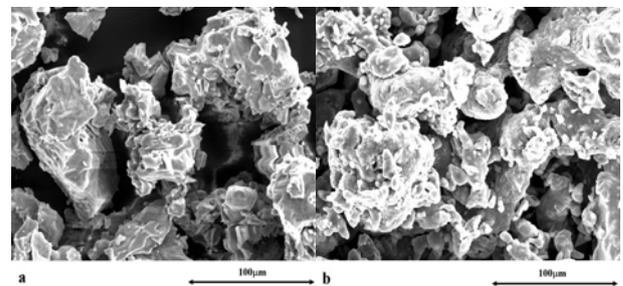
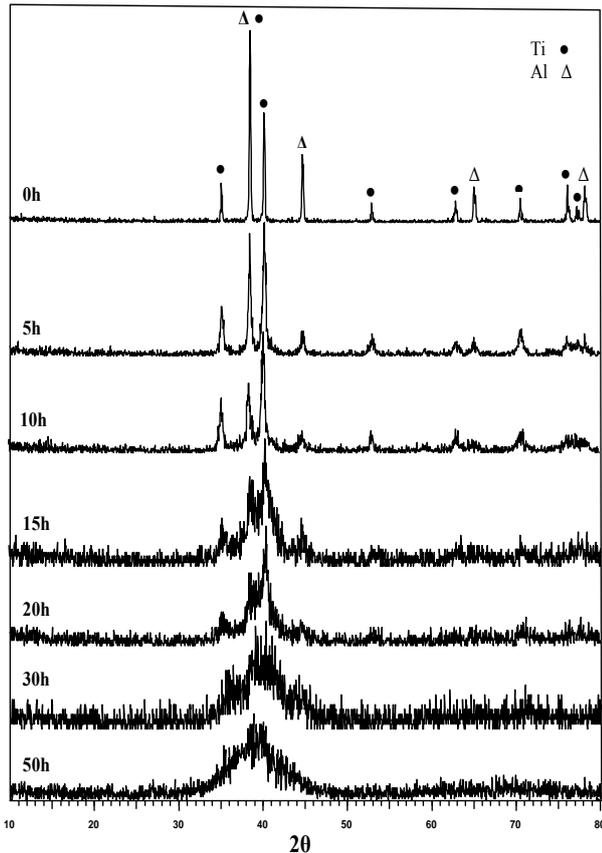
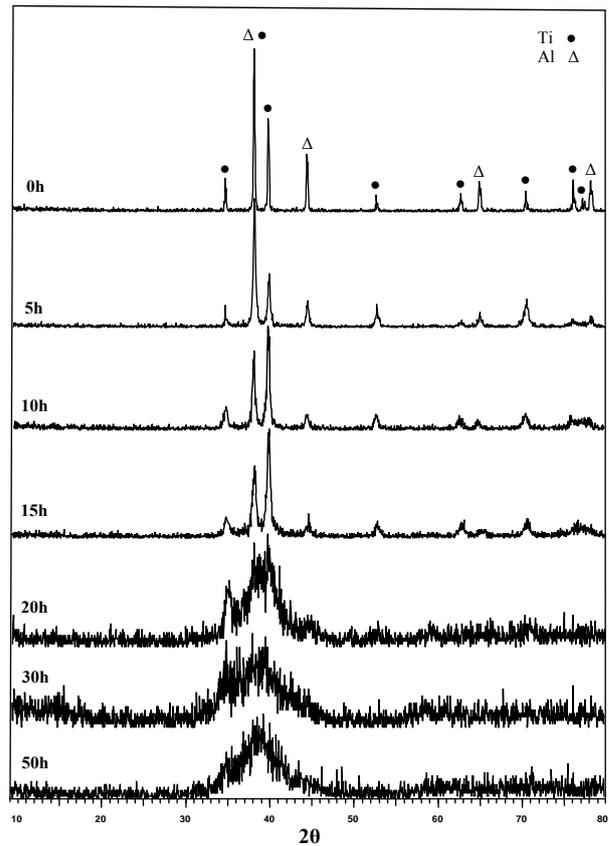


Figure 2. SEM micrographs of pure (a)Ti (b)Al.



**Figure 3.** X-ray diffraction patterns of  $Ti_{50}Al_{50}$  elemental powder, mechanically alloyed at several alloying times and with 2wt% Methanol.



**Figure 4.** X-ray diffraction patterns of  $Ti_{50}Al_{50}$  elemental powder, mechanically alloyed at several alloying times with 2wt% Stearic acid.

The crystallite size and lattice strain of the powder particles were determined using the X-ray *peak broadening techniques* (Scherrer and Williamson-Hall formulas):

$$d = \frac{0.9\lambda}{B \cos \Theta}$$

$$B \cos \Theta = \frac{0.9\lambda}{d} + \eta \sin \Theta$$

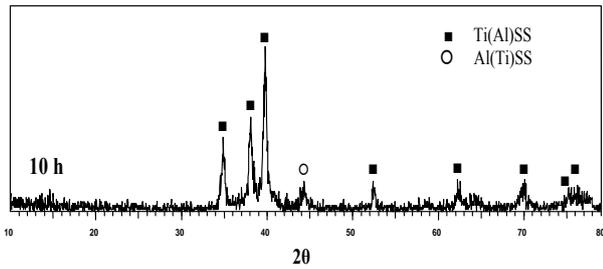
Where  $d$  is the crystallite size,  $\lambda$  is the wavelength of the X-radiation used,  $B$  is the peak width at half the maximum intensity,  $\Theta$  Bragg angle and  $\eta$  is the strain [17]. Some samples were examined after mechanical treatment by differential thermal analysis (DTA) L62 HDSC. This test performed in argon atmosphere. Annealing of samples was executed by Alcatel CFA-222 vacuum furnace.

### 3. RESULTS AND DISCUSSION

SEM images of pure Ti and Al powders are shown in Fig. 2.

XRD patterns of  $Ti_{50}Al_{50}$  powder, mechanically alloyed with 2wt% methanol and stearic Acid for several alloying times are shown in Figs.3 and 4 respectively.

The XRD patterns showed that the diffraction intensities drastically decreased and broadened after 5h milling time. The diffraction peaks corresponding to the Al disappeared at an early time, indicating the solution of Al in Ti lattice. In Fig. 3 after 10h milling, the metastable solid solution of Al in Ti (hcp disordered) phase and a small amount of metastable solid solution of Ti in Al were formed (Fig. 5). The diffusion of Al in Ti lattice is faster than that of Ti in Al lattice [17].



**Figure 5.** X-ray diffraction patterns of  $Ti_{50}Al_{50}$  elemental powder, mechanically alloyed after 10h alloying time and with 2wt% Methanol.

When stearic acid was used as a PCA, the metastable phase formed after 15h alloying time.

In both cases, the diffraction intensities of Ti decreased gradually with increasing the time of milling and observation of shifts in the diffraction angles of Ti to higher angles indicated the formation of a solid solution of Al in Ti and shrinkage of lattice parameters of Ti [18, 19].

The different time between the formation of metastable phase with two different PCA is because of the solid state of stearic acid that needs primary energy to melt and be more effective at alloying process.

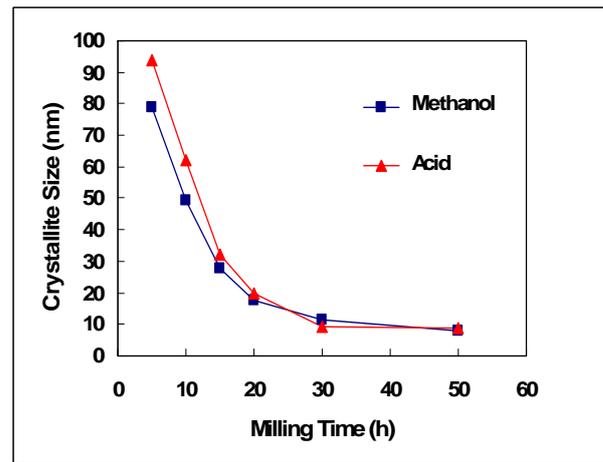
Until the stearic acid melted completely, the particles of powders tended to stick to each other, but methanol is liquid and at early time of mechanical alloying, it is more effective in fracturing the particles and accelerate the diffusion process.

The diffraction peaks around  $2\theta=40^\circ$  can not be separated after an alloying time of 30h.

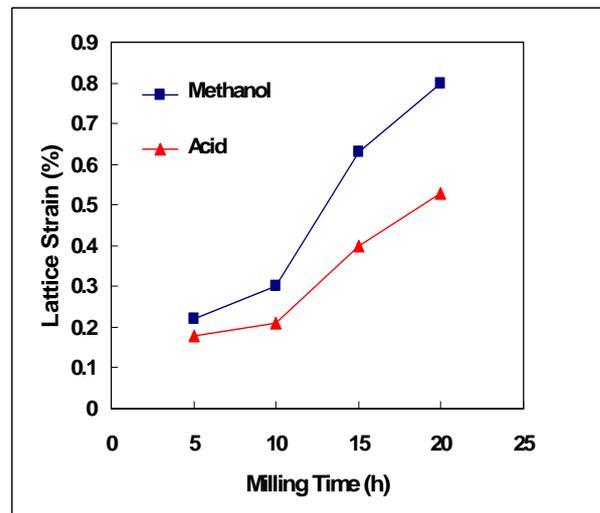
The formation of an amorphous-like phase or very fine particles has been strongly enhanced with increasing of milling time [17, 18]. Amorphization during MA is a result of increasing the free energy of system. The continuous decrease in grain size (and consequent increase in grain boundary area) and a lattice expansion would also contribute to the increase in free energy of the system [17]. In both cases, that phase was formed completely after 50h.

The rate of alloying process in samples with methanol were faster than stearic acid because of the nature of PCA, its characteristic and advantage of liquid form of methanol than solid form of stearic acid.

The grain size and lattice strain of Ti as a function



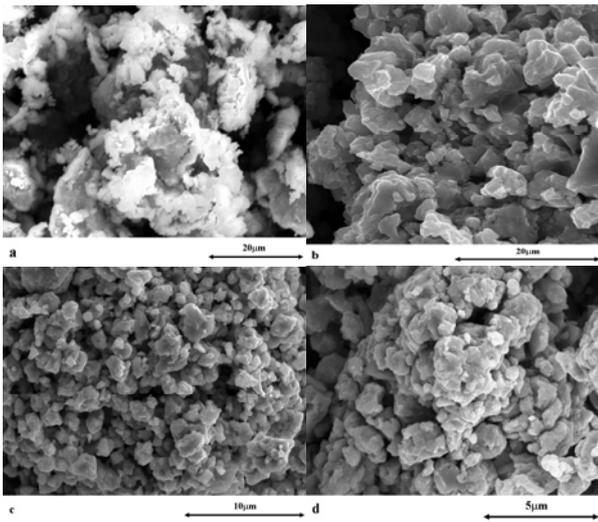
**Figure 6.** The average grain size of productions of M.A process as a function of alloying time for two PCA.



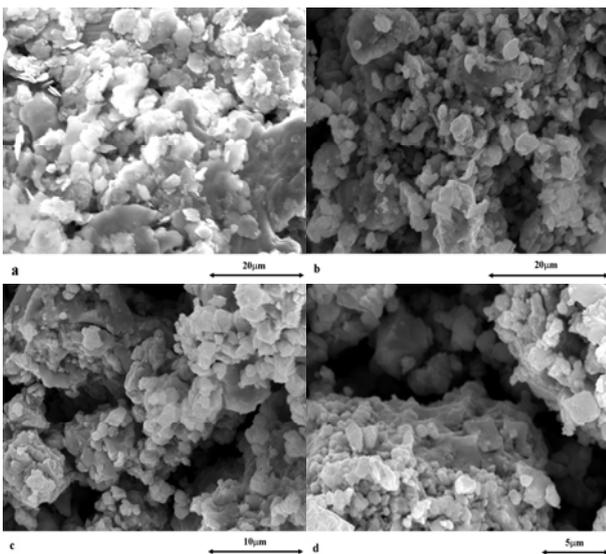
**Figure 7.** The lattice strain of productions of M.A process as a function of alloying time for two PCA.

of milling time for two PCA are shown in Figs. 6 and 7, respectively. The lattice strain of Ti was increased and grain size was decreased with increasing milling time because the impact energy of the balls which exerted on powder particles increased with increasing the milling time further.

At primary time of alloying, the decreasing rate of grain size was extreme and corresponding to Fig. 6 after 15h of milling; this rate decreased because of two reasons, 1) small particles able to withstand extra deformation and 2) the balance achieved between the rate of welding and



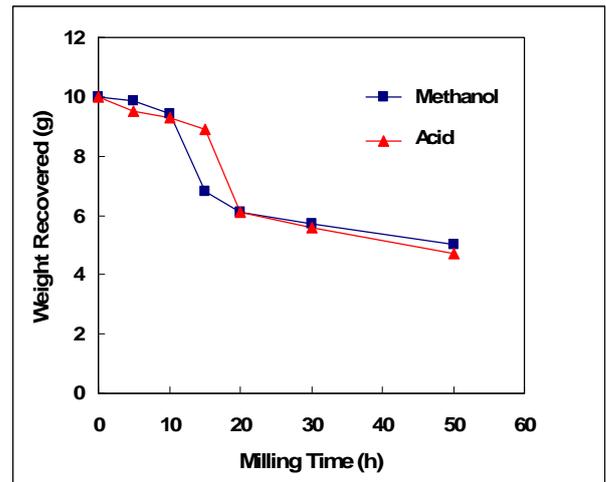
**Figure 8.** SEM micrographs of  $Ti_{50}Al_{50}$  powders mechanically alloyed after (a) 5h (b) 20h (c) 30 and (d) 50h with 2%wt Methanol.



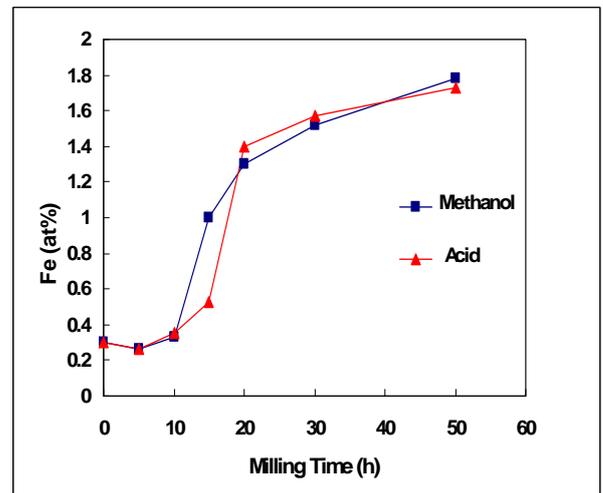
**Figure 9.** SEM micrographs of  $Ti_{50}Al_{50}$  powders mechanically alloyed after (a) 5h (b) 20h (c) 30 and (d) 50h with 2%wt stearic acid.

fracturing after specific alloying time [13, 17].

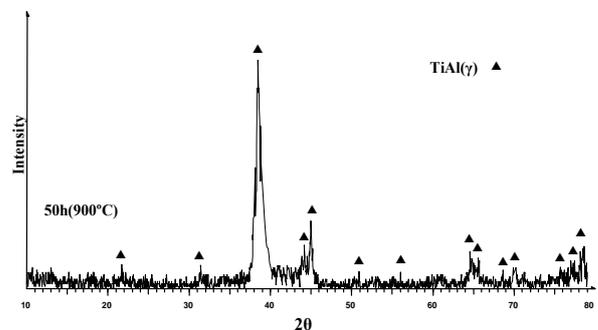
Before 15h of milling when stearic acid was used as a PCA, the decreasing rate of grain size was faster than methanol was used because methanol was liquid and more effective in decreasing the rate of fracturing at early alloying time.



**Figure 10.** The weight recovered of production of process as a function of time for two PCA.



**Figure 11.** The Fe contamination of productions of process as a function of time for two PCA.



**Figure 12.** XRD pattern of mechanically alloyed  $Ti_{50}Al_{50}$  after annealed at 900°C for 10min at vacuum oven.

Corresponding to Fig. 7, when stearic acid was used, the increasing rate of strain was less than when methanol was employed because methanol was more effective in decreasing the rate of cold welding at early time that caused distribution strain to more fractured particles.

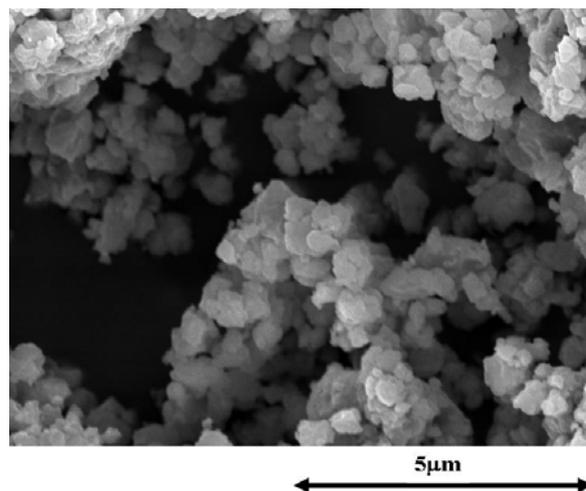
SEM images of  $Ti_{50}Al_{50}$  powders that mechanically alloyed at several alloying times with methanol and stearic acid are shown in Figs. 8 and 9 respectively.

These images indicated that, methanol (liquid state) is adsorbed on the surface of the particles easily and minimizes the cold welding at first time of M.A. In this case, the rate of fracturing dominated on cold welding at primary hours of milling. In samples with stearic acid we observed the large particles at 5h of alloying time because stearic acid did not melt perfectly and the large particles were achieved that showed the domination of cold welding on fracturing at primary hours. In both cases, after alloying for certain length of time, a balance was achieved between the rate of cold welding and fracturing. At the last stages of M.A, the particles tended to agglomerate, probably due to the lack of PCA at the end of M.A process. In both cases we observed the change of the particle size from micro-nano size.

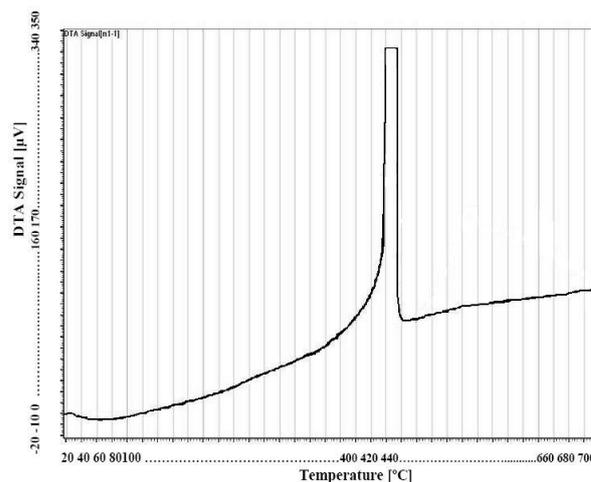
The recovered weight and Fe contamination as a function of milling time for two PCA is shown in Figs. 10 and 11.

When methanol and stearic acid was used as a PCA, after 10h and 15h alloying, respectively, the weight recovered was decreased significantly. Sticking tendency to milling tools caused this change. According to XRD patterns, it seems that when powder mixture transformed to Ti solid solution phase gradually, sticking tendency to milling tools were increased thus the weight recovered was decreased.

In both cases, the Fe contamination showed a little change at first time of alloying. In samples with methanol, from 10 to 15h and in samples with stearic acid, from 15 to 20h alloying, the Fe concentration increased obviously. Sticking of powder mixture to milling tools and increased collision between balls-powder-vial are the factors have effect on this case.



**Figure 13.** SEM micrographs of mechanically alloyed  $Ti_{50}Al_{50}$  sample after annealed at  $900^{\circ}C$  for 10min at vacuum oven.



**Figure 14.** The curve of DTA test for 50h sample.

When the energy of milling was lower, the difference between the application of methanol and stearic acid as a PCA was obvious. With increasing the milling energy (by increasing the rotation speed or ball-to-powder weight ratio) the influence of this difference decreased because the high energy of milling melt the stearic acid very quickly and speed up the process.

Finally, with annealing the final product of process in vacuum furnace for 10min at  $900^{\circ}C$ , the

TiAl( $\gamma$ ) phase with high purity and 25nm average grain size was produced (Figs. 12 and 13).

The result of DTA test on this sample showed an exothermic peak around 450°C. This temperature is due to crystallization of an amorphous TiAl to crystalline TiAl( $\gamma$ ) (Fig. 14).

#### 4. CONCLUSION

-The diffraction intensities of Ti and Al decreased and broadened during mechanical alloying. It seems, the strain caused by collisions of balls, the decrease in the grain size of powder particles and the increase in the density of defects are the reasons of broadened the diffractions.

- The Al diffractions disappeared quickly as a result of the solution of Al in Ti lattice and formation of metastable solid solution Al in Ti phase (hcp disordered).

- At the presence of methanol as a PCA, the S.S phase formed after 10h milling time and at the presence of stearic acid the metastable phase formed after 15h alloying.

- When methanol was used as a PCA, the rate of alloying process was faster than when stearic acid was used, because of the nature of PCA, its characteristic and advantage of liquid form of methanol compared to solid form of stearic acid.

- It seemed, when Ti solid solution phase was formed gradually, the sticking tendency to milling tools increased, thus the weight recovered decreased.

- Increasing the time accelerated the formation of the amorphous phase.

#### 5. REFERENCES

1. K. R. Cardoso, C. A. D. Rodrigues, "Processing of Aluminium Alloys Containing Titanium addition by Mechanical Alloying", *Materials Science and Engineering A*, vol. 375, (2004), 1202-1207.
2. Z. M. Sun, H. Hashimoto, "Fabrication of TiAl alloys by MA-PDS process and mechanical properties", *Intermetallics*, vol. 11, (2003), 826-830.
3. K. Uenishi, T. Marsobara, "Nanostructured Titanium-Aluminides and Their Composites Formed by Combustion Synthesis of Mechanically Alloyed Powders", *Scripta Materialia*, vol. 44, (2001), 2094-2098.
4. S. H. Kim, H. H. Chung, "Effect of B on the Microstructure and Mechanical Properties of Mechanically milled TiAl Alloys", *Metallurgical and Materials Transaction A*, vol. 20, (1998), 2273-2276.
5. E. Szewczak, J. Paszula, A. V. Lenov and H. Matyja, "Explosive Consolidation of Mechanically Alloyed Ti-Al Alloys", *Materials Science and Engineering A*, vol. 226, (1997), 115-118.
6. S. Dymek, M. Wrobel, "Effect of 5at% Addition of Cr, V and W on Microstructure and Mechanical Properties of  $\gamma$ -TiAl Based Alloys", *Archives of Metallurgy and Materials*, Vol. 5, (2006), 97-101.
7. L. Lu, M. O. Lai and F. H. Froes, "The Mechanical Alloying of Titanium Aluminides", *JOM*, vol. 54, (2002), 62-66.
8. C. Suryanarayana, "Recent Developments in Mechanical Alloying", *Rev. Adv. Mater. Sci.*, vol. 18, (2008), 203-211.
9. E. Paransky, E. Y. Gutmanas, I. Gotman and M. Koczek, "Pressure Assisted Reactive Synthesis Of Titanium Aluminides From Dense 50Al-50Ti Elemental Powder Blends", *Metallurgical and Materials Transaction A*, vol. 27, (1996), 2130-2135.
10. S. C. Tjong and Hayden Chen, "Nanocrystalline Materials and Coatings", *Materials Science and Engineering R*, vol. 45, (2004), 14-36.
11. F. H. Froes, C. Suryanarayana, K. Russel and C. G. Li, "Synthesis of Intermetallics by Mechanical Alloying", *Materials Science and Engineering A*, vol. 192, (1995), 612-623.
12. Y. Mishin, Chr. Herzig, "Diffusion in the Ti-Al system", *Acta Materials*, vol. 48, (2000), 591-562.
13. M. Sherif El-Eskandarany, "Mechanical Alloying for Fabrication of Advanced Engineering Materials", William Andrew Publication, USA, (2001).
14. L. Shaw, M. Zawarach, "Effect of Process-control\_agent on Mechanical Alloying of Nanostructured Alluminum Alloys", *Metallurgical and Materials Transactions A*, vol. 34, (2003), 159-166.
15. Y. F. Zhang, L. Lu and S. M. Yap, "Prediction of The Amount of PCA for Mechanical Milling", *Materials Processing Technology*, vol. 89-90, (1999), 260-264.
16. S. Kleiner, F. Bertocco, F. A. Khalid and O. Beffort, "Decomposition of Process Control Agent During Mechanical Milling and Its Influence On Displacement Reactions In The Al-TiO<sub>2</sub> System", *Materials Chemistry and Physics*, vol. 89, (2005), 362-366.
17. C. Suryanarayana, "Mechanical Alloying and Milling", *Progress in Materials Science*, vol. 46, (2001), 100-140.
18. L. Lu, M. O. Lai, "Mechanical Alloying", Kluwer Academic Publishers, Boston, (1998).
19. Akito Takasaki, Yoshio Furuya, "Mechanical Alloying of The Ti-Al System in Atmosphere of Hydrogen and Argon", *Nanostructured Materials*, vol. 11, (1999), 1209-1212.