The Effect of Impurity of Inert Atmosphere on Synthesis of Nanostructure TiAl (γ) Alloy by Mechanical Alloying Process

F. Abbasi Nargesi*, R. Azari Khosroshahi, N. Parvini Ahmadi

Matrials Engineering Faculty, Sahand University of Technology, Tabriz, I. R. Iran

(*) Corresponding author: farshadabbasi60@yahoo.com
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Abstract:
In this research, the high-energy planetary mill was employed to produce nanocrystalline Ti-50Al(γ)(at%) powders. Initial powders were mechanically alloyed in 99.9999% and 90% purities of Argon and also Air atmosphere with alloying times up to 50h. The effect of impurity of Argon atmosphere on the microstructure and the rate of phase transformation of Ti-50Al were investigated during mechanical alloying and after annealing at 1000°c. The results showed that the formation of nanostructure TiAl(γ) phase had directly related to the impurities of atmosphere in vials. The impurity of the atmosphere could delay the rate of amoprphization during mechanical alloying and decrease the rate of mechanical alloying process beside some unwanted phases which were produced in powder mixture. The powder particles produced in the high purity Argon atmosphere seemed to be finer than those in the atmosphere. The X-ray patterns, SEM analysis, changes in grain size and DTA test were studied during mechanical alloying and after annealing.
Keywords: *Titanium Alumindes, Mechanical Alloying, Nanostructure, Atmosphere, Impurity.*

1. INTRODUCTION

TiAl based alloys are considered as promising structural materials for high temperature aerospace and automotive applications. This is essentially due to some attractive properties such as low density, high specific strength, high specific stiffness and high temperature strength retention [1-4].
However, two major drawbacks remain: brittleness and poor formability at low temperature [4-6].
Many attempts have been made during recent decades to overcome these obstacles; one of them is grain refinement (to nanometer-sized grains). Mechanical alloying has been used to refine the grain size and synthesize non-equilibrium structures [6-8].
The mechanical alloying process is a solid state powder process where the powder particles are subjected to high energetic impact by the balls in vial. As the powder particles in the vial are continuously impacted by the balls, cold welding between particles and fracturing of the particles repeatedly take place during the ball milling process [9-12].
For the alloying process, several control parameters have to be considered, namely, environment in the vial, ball to powder weight ratio and process control agent.
The major effect of the milling atmosphere is on the contamination of the powder. Therefore, the powders are milled in containers that have been either evacuated or filled with an inert gas such as Argon or Helium. High-purity argon is the most common ambient to prevent oxidation and/or contamination of the powder. The type of atmosphere also seems to affect the nature of the final phase [12-15].

The aim of the present work is to study the effect of Argon atmosphere purity on the microstructure of Ti-50Al alloy during mechanical alloying and after annealing at 1000°C for 10min at vacuum furnace.

2. EXPERIMENTAL PROCEDURE

Titanium and aluminum of more than 99.5% purity and particle size 100-150μm were used as starting powders to reach Ti-50Al(at%) (γ). The powders weighed in a glove box with argon atmosphere. The FP4 planetary mill with two tempered steel bowels with steel balls was employed in this research. The capacity of each vial was 250ml. The diameters of balls were 15 and 20 mm. The vials were designed to allow pumping and subsequent filling by an inert gas. Argon atmosphere with 99.9999% and 90% purities and also air atmosphere were studied in this research. The final gas pressure in the vial was kept to be 0.1 Mpa. Methanol was used as a process control agent (PCA). 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 increase, 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_α radiation at 30kv and 20 mA. Analyses of the powder morphology and particle size measurements were achieved by Cam Scan MV-2300 SEM with EDS analyzer at an accelerating voltage of 25Kv.
The crystallite size and lattice strain of the powder particles were determined using the X-ray peak broadening techniques (Scherrer and Williamson-Hall formulas):

$$d = \frac{0.9\lambda}{B\cos\theta} \qquad (1)$$

$$B\cos\theta = \frac{0.9\lambda}{d} + \eta\sin\theta \qquad (2)$$

d is the crystallite size, λ is the wavelength of the X-radiation used , B is the peak width at half the maximum intensity, θ Bragg angle and η is the strain. 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

XRD patterns of Ti-50Al (at%) powder blends that mechanically alloyed in high purity Argon (99.9999%) atmosphere for several alloying times are shown in Figure 1.

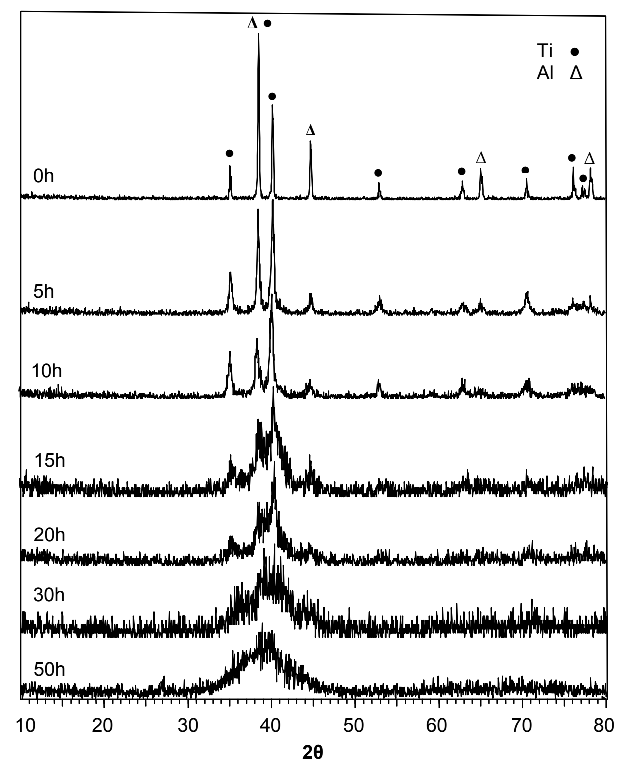

Figure 1: *X-ray diffraction patterns of Ti-50Al (at%) elemental powder, mechanically alloyed at several alloying times in high purity Argon atmosphere (99.9999%).*

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 Figure 1, the metastable solid solution of Al in Ti phase and a little metastable solid solution of Ti in Al were formed after 10h milling.

Al is diffused faster in Ti lattice in comparison to Ti in Al lattice [16-18].

The diffraction intensities of Ti is gradually decreased 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. The lattice parameters of the α-Ti after M.A for 10h are approximately a=0.255nm and c=0.467nm whereas those before M.A are approximately a=0.258nm and c=0.470nm so that about 2% volume shrinkage has occurred which was due to the diffusion of Al into Ti lattice that promotes the Ti(Al) solid solution.

During mechanical alloying in high purity of Argon atmosphere, the oxide or nitrogen compounds were not seen in powder mixture.

Moreover, the diffraction peaks around 2θ=40º can not be separated after an alloying time of 30h.

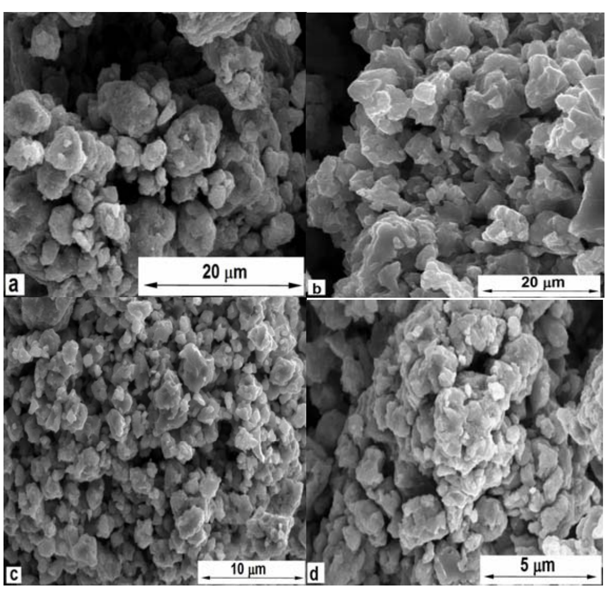

Figure 2: *SEM micrographs of Ti-50Al powder blends that mechanically alloyed after (a)10h (b)20h (c)30 and (d)50h in high purity Argon Atmosphere.*

The formation of an amorphous-like phase or very fine particles has been strongly enhanced with increasing the milling time. Amorphization during MA, as 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 [16, 17].

The amorphous phase and very fine particle was completely formed after 50h milling.

SEM images of Ti-50Al powders that mechanically alloyed at several alloying times in high purity Argon are shown in Figure 2.

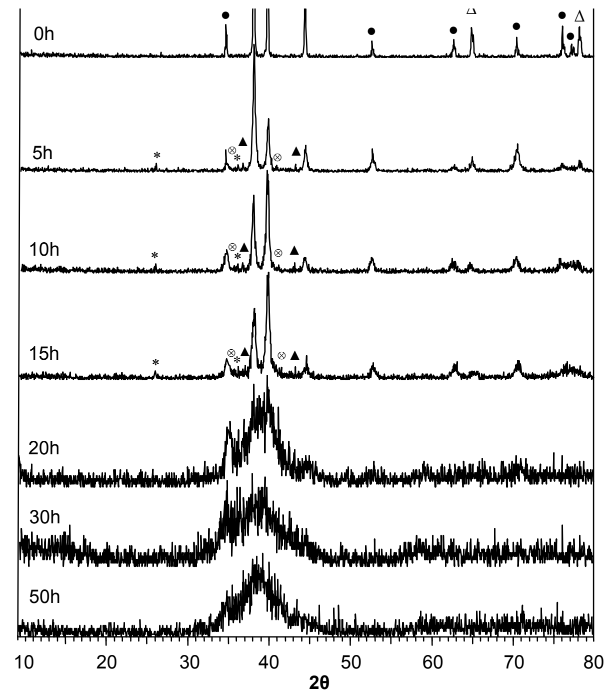

Figure 3: *X-ray diffraction patterns of Ti-50Al elemental powder, mechanically alloyed at several alloying times in 90% purity of Argon atmosphere.*

These images indicated that with increasing the alloying time, the particle size of the powder were decreased and the homogenous and very fine particles were achieved after 50h alloying time.

XRD patterns of Ti-50Al powder blends that mechanically alloyed for several alloying times in 90% purity of Argon and air atmosphere are shown in Figures 3 and 4 respectively. When the purity of atmosphere decreased to 90%, some compositions such as TiO_2, Al_2O_3 and TiH_2 were appeared in X-ray patterns. When air atmosphere was used in the vials, the contaminations such as TiN, Ti_2AlN, TiO_2, Al_2O_3, TiH_2 were seen in XRD patterns. In this case, we couldn't see an entire broad peak that indicated a complete amorphous phase after 50h

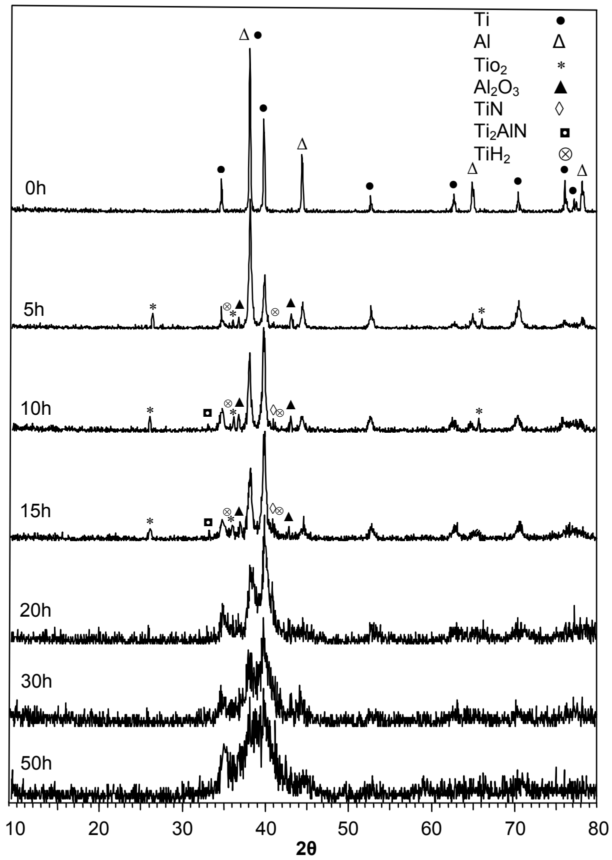

Figure 4: *X-ray diffraction patterns of Ti-50Al elemental powder, mechanically alloyed at several alloying times in Air atmosphere.*

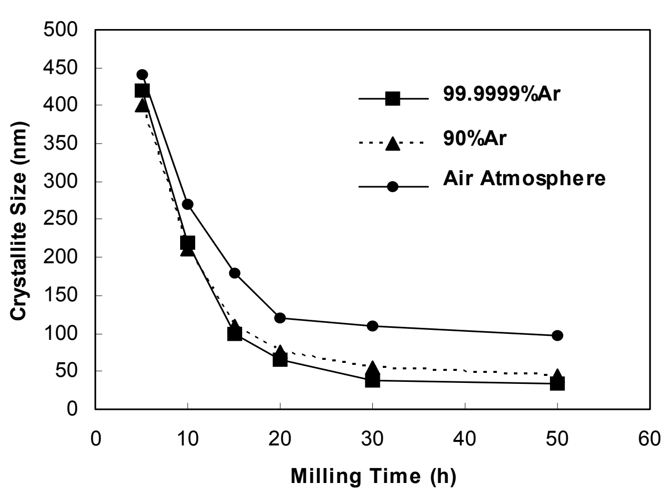

Figure 5: *The average grain size of productions of M.A process as a function of milling time for three atmospheres.*

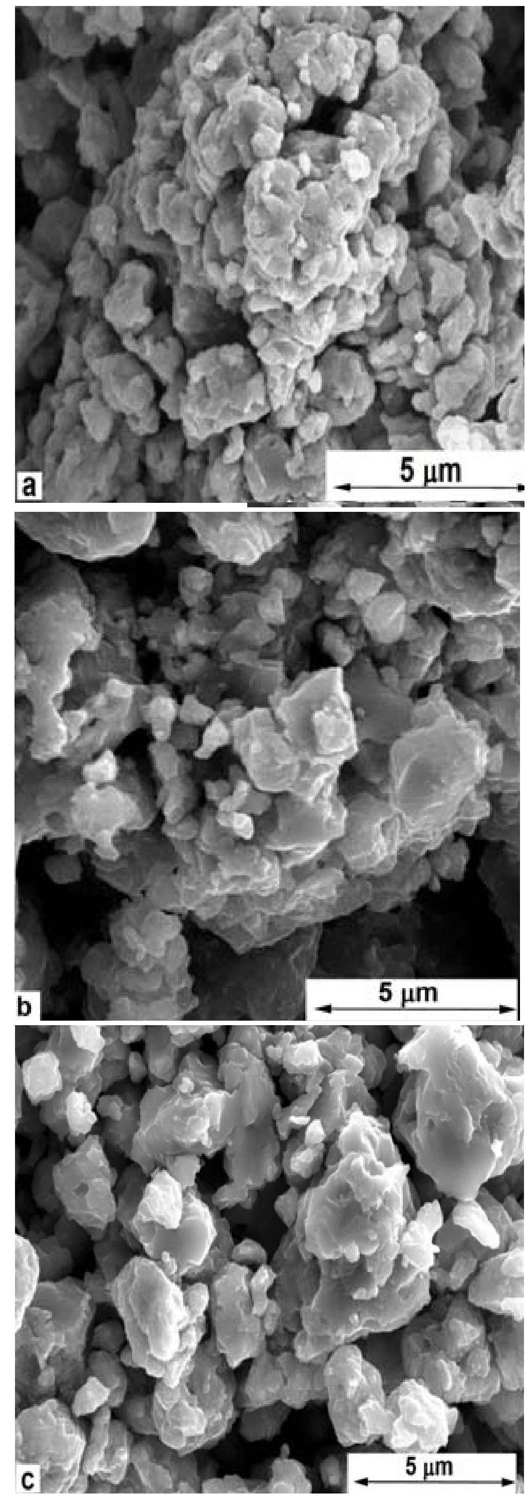

Figure 6: *SEM micrographs of Ti-50Al powders mechanically alloyed after 50h in (a)high purity Argon atmosphere(99.9999%) (b)90% Argon atmosphere (c) Air atmosphere.*

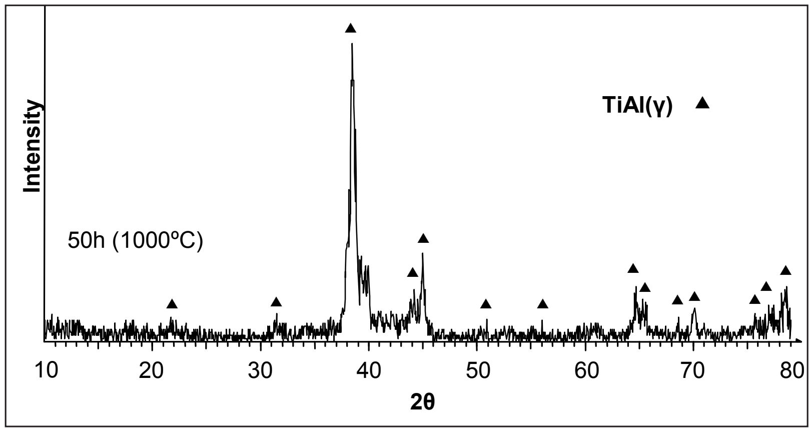

Figure 7: *XRD diffraction pattern of Ti-50Al which mechanically alloyed in high purity Argon atmosphere after annealed at 1000ºc for 10min at vacuum furnace.*

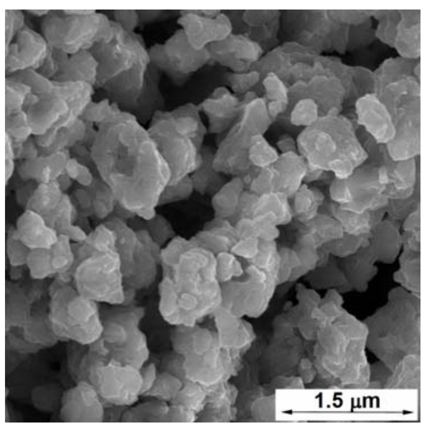

Figure 8: *SEM micrographs of last mechanically alloyed Ti-50Al sample in high purity Argon atmosphere, after annealed at 1000ºc for 10min at vacuum oven.*

alloying time.

By comparing these XRD patterns, it seemed that the time to reach a complete amorphous phase was decreased with increasing the impurity of atmosphere of vials.

It suggests that contaminative phases such as oxides and nitrides can delay the rate of mechanical alloying process.

In mechanical alloying method, 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. During alloying when contaminations were produced, these compounds can place between the fine particles and delay the diffusion mechanism of the process.

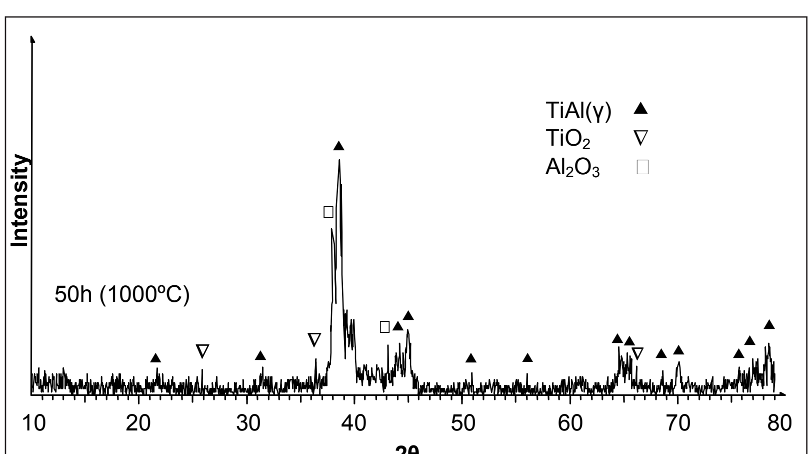

Figure 9: *XRD diffraction pattern of Ti-50Al which mechanically alloyed in 90% purity Argon atmosphere after annealed at 1000ºc for 10min at vacuum furnace.*

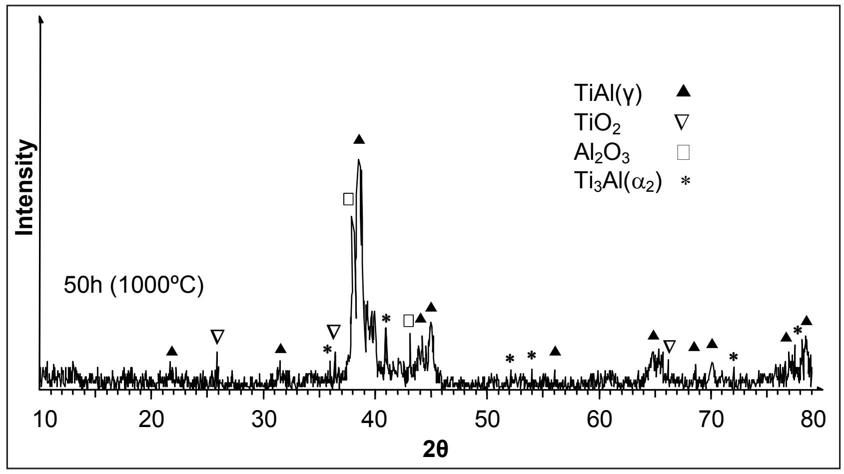

Figure 10: *XRD diffraction pattern of Ti-50Al which mechanically alloyed in Air atmosphere after annealing at 1000°c for 10min at vacuum furnace.*

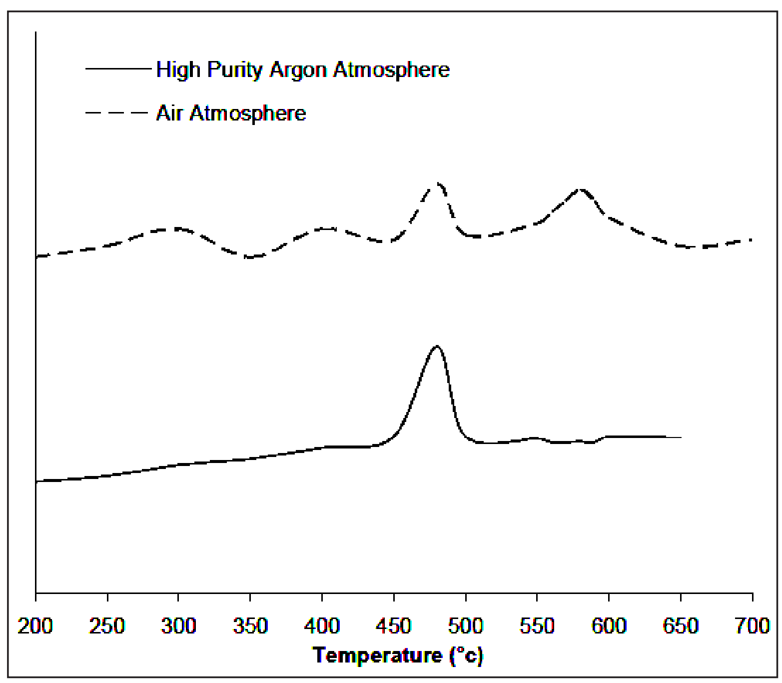

Figure 11: *The curve of DTA test for two different atmosphere samples.*

The grain size of Titanium as a function of milling time for three employed atmosphere are shown in Figure 5.

It seems that the grain sizes of powders in samples with high purity of Argon are a little smaller than those in other atmospheres.

Figure 6 compared the SEM images of the powders, mechanically alloyed for 50h in three different atmospheres.

SEM images, confirmed the results of Figure 5. The powder particles produced in the high purity Argon atmosphere seems to be finer than those in the atmosphere which have impurities. The elemental powders might react better in a high purity atmosphere than in other atmospheres.

Finally, with annealing the last productions of process in vacuum furnace for 10min at 1000°c, the final phases were formed. In sample that mechanically alloyed in high purity Argon, the TiAl(γ) phase with very high purity and 50nm average grain size was produced (Figure 7). This phase was our ideal phase corresponding to Ti-Al binary diagram. SEM image of this sample is also shown in Figure 8.

For the samples which mechanically alloyed in 90% purity of Argon and air atmosphere, the final phase after annealing contain TiAl(γ) and other phases such as $Ti_3Al(\alpha_2)$ and other contaminations such as TiO_2, Al_2O_3 (Figures 9 and 10).

When the impurity of atmosphere was increased, the γ phase content was reduced, the intensity of γ peaks were lowered and other contaminations were increased in the final powder mixture. Some phases such as TiH_2, TiN were disappeared after annealing in vacuum furnace.

Figure 11 compared the results of DTA test for samples that mechanically alloyed in high purity argon and air atmosphere after 50h alloying times.

The result of DTA test on the sample which mechanically alloyed in high purity Argon atmosphere showed an exothermic peak around 450ºc.

This temperature concern to crystallization of an amorphous TiAl to crystalline TiAl(γ) phase but for other sample that mechanically alloyed in Air atmosphere, besides of this exothermic peak, the peaks around 570 ºc which concern to $Ti_3Al(\alpha_2)$ and other peaks concern to other contaminations such as TiO_2, Al_2O_3 were revealed.

4. CONCLUSION

- When a very high purity of Argon atmosphere were used in vials, the time to formation of amorphous phase was decreased and only γ phase was produced which has no contamination after annealing.
- Increasing the impurity content of atmosphere, delayed the time to formation of an amorphous phase in Ti-50Al system.
- With increasing the impurity of atmosphere, the content of contaminative phases and compounds were accelerated during mechanical alloying of Ti-50Al powder mixture.
- Powder particles synthesized in the high purity Argon atmosphere seems to be finer than those in the atmosphere which had impurities.
- The impurity of atmosphere changed the final phases of Ti-50Al after annealing and reduced the efficiency of γ-TiAl production.

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