SYNTHESIS OF NANOSTRUCTURE Ti-45Al-5Cr ALLOY BY MECHANICAL ALLOYING AND STUDY THE EFFECT OF Cr ADDITION ON MICROSTRUCTURE OF TiAl ALLOY

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

Department of Materials Engineering, Sahand University of Technology
P.O. Box 51335-1996, Tabriz, Iran
farshadabbasi60@yahoo.com - rakhosroshahi@sut.ac.ir - parvini@sut.ac.ir

*Corresponding Author

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Abstract In this work, mechanical alloying was employed to produce Ti-50Al and Ti-45Al-5Cr (at %) alloys. Alloying was performed in a planetary mill and the alloying time varying from 5 to 70 h. Characterization of the powder mixture was performed by X-ray diffraction (XRD) technique, Scanning Electron Microscopy (SEM) and Differential Thermal Analysis (DTA), during mechanical alloying and after annealing treatment at 1100˚C in vacuum furnace. The results showed, only a complete amorphous phase was detected after 50h of milling of Ti-50Al powder blends but with 5 at % addition of Cr, the Cr (Ti, Al) solid solution phase within the amorphous matrix were formed. While annealing of the mechanically alloyed Ti-50Al powders at 1100˚C for 10min leads to the nanocrystalline phase of TiAl(γ), nanocrystalline phases of mainly Ti Al(γ) together with $Ti_3Al(\alpha_2)$ were formed in Cr containing powders. Cr accelerated the production of duplex structure ($\gamma+\alpha_2$) and It seemed that the Cr (Ti, Al) solid solution was dissolved in TiAl(γ) and $Ti_3Al(\alpha_2)$.

Keywords Mechanical Alloying, Titanium Aluminide, Chromium, Nanostructure

چکیده در این کار، آلیاژسازی مکانیکی برای تولید آلیاژهای Ti-50Al و Ti-45Al-5Cr (درصد اتمی) مورد استفاده قرار گرفت.آلیاژسازی در آسیاب سیاره ای انجام پذیرفت و زمان آلیاژسازی از ۵ تا ۷۰ ساعت متغیر بود. مشخصه یابی مخلوط پودری بوسیله تکنیک پراش اشعه ایکس(XRD)، میکروسکوپ الکترونی روبشی (SEM) و آنالیز تفاضلی حرارتی(DTA) در طول آلیاژسازی مکانیکی و پس از آنیلینگ در دمای ۱۱۰۰ درجه سانتیگراد در کوره خلا انجام پذیرفت. نتایج نشان داد پس از آسیاب مخلوط پودری Ti-50Al به مدت ۵۰ ساعت، تنها یک فاز کاملاً آمورف شناسایی شد ولی با افزودن ۵ درصد اتمی کروم، محلول جامد تیتانیوم و آلومینیوم در کروم همراه با فاز آمورف تشکیل شد. درصورتیکه با آنیل پودرهای آلیاژسازی مکانیکی شده Ti-50Al در ۱۱۰۰ درجه سانتیگراد به مدت ۱۰دقیقه منجر به فاز نانوساختار TiAl(γ) شد و فاز نانوساختار TiAl(γ) همراه با $Ti_3Al(\alpha_2)$ در پودرهای حاوی کروم تشکیل شد. کروم تولید ساختار دوفازی($\gamma+\alpha_2$) را تسریع نمود و به نظر رسید که محلول جامد آلومینیوم و تیتانیوم در کروم در TiAl(γ) و$Ti_3Al(\alpha_2)$ حل گردید.

1. INTRODUCTION

Titanium Aluminide intermetallic compounds, especially the γ-base TiAl alloys are potentially suitable as advanced structural materials for high performance applications such as components in aircraft turbine engines, aerospace vehicles and automotive engines due to low density, high strength and high elastic modulus, excellent creep and oxidation resistance [1-6]. However, their general lack of ambient temperature ductility and high temperature creep resistance has led to a number of alloy design paths being pursued for improvement of their properties [6-8].

Different methodologies have been followed to attempting to increase the ductility of the ordered phase γ-TiAl; (1) The use of new processing technique such as mechanical alloying for microstructure refinement and for obtaining material which is high homogeneous in structure and compositions. (2) Addition of alloying element such as Cr, W, Nb, …, to produce the duplex structure($\gamma+\alpha2$) [9-11].

Mechanical alloying is a proper process to production of ultra fine grain and nanocrystalline TiAl products. The larger fraction of grain boundaries is expected to lead to diffusion controlled deformation mechanisms and an improvement in ductility [12-15].

The best comprise between high temperature properties and room temperature ductility is achieved with a two-phase microstructure ($\gamma+\alpha 2$). This compromise is often achieved by decreasing the aluminum Content of the alloy and adding small amount of alloying elements such as Cr, Mn, W and B which were found to refine the grain size and stabilize the duplex structure [15-17].

During recent years extensive research has been carried out to develop two phase base alloys consisting of γ-TiAl and α2-Ti3Al for structural applications. The most promising alloys are based on Ti-(45-48 % at) Al compositions with ternary or quaternary additions. The properties of these alloys are quite sensitive to microstructure [18-20].

Combine the production of nanostructure grain size of the alloy and achieve the duplex phase ($\gamma+\alpha 2$) in the microstructure of the alloy are the best condition to overcome the obstacles of the single phase γ-TiAl alloy.

This research was aimed on the production of Ti-50 Al and Ti-45Al with Cr addition (Ti-45Al-5Cr). The effect of Cr on the microstructure of Ti-Al system during mechanical alloying and after annealing at 1100°C in vacuum furnace was investigated.

2. EXPERIMENTAL PROCEDURE

Elemental powders of high purity 99.8 % Ti (size under 80 μm), 99.7 % Al (size under 75 μm) and 99.5 % Cr (size under 50.9 μm) were used as the starting reactant materials. The powders were initially mixed and weighted to prepare a composition of Ti-50Al and Ti-45Al-5Cr (in at %) in a glove box with argon atmosphere. The mixing and alloying were carried out at room temperature in the FP4 planetary mill at a rotation speed of 500rpm. The vials and milling media were made from tempered steel. The diameters of balls were 15, 20 mm. The vials were designed to allow pumping and subsequent filling by an inert gas (Ar) with high purity (99.9999 %). The final gas pressure in the vial was kept to be 0.1 Mpa. 1 wt % of Methanol was added to avoid the sticking of powders to milling media. The ball-to-powder weight ratio was 15:1. The maximum alloying time accumulated was 70 h. After alloying for various lengths of time up to 70h, the milled powders were withdrawn from vials for subsequent analysis.

The crystal structure of the powders was characterized by a Bruker-D8-Advanced, using Cu-Kα radiation at 30 kv and 20 mA. Analysis of the powder morphology and particle size measurements was achieved using a Cam Scan MV-2300 SEM equipped with an EDS analyzer at an accelerating voltage of 25 Kv.

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

$$d = \frac{0.9\, l}{B \cos \Theta}$$

$$B \cos \Theta = \frac{0.9\, l}{d} + h \sin \Theta$$

where 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

SEM micrographs of pure Ti, Al and Cr powders are shown in Figure 1. All starting elemental powders have irregular shapes.

In order to study the effect of Cr on kinetic of structural changes during MA process, two compositional Ti-50Al and Ti-45Al-5Cr powder blends were mechanically alloyed for different times.

In Ti-50Al powder mixture the diffraction intensities drastically decreased and broadened after 5h alloying time. The diffraction peaks corresponding to the Al, disappeared at an early

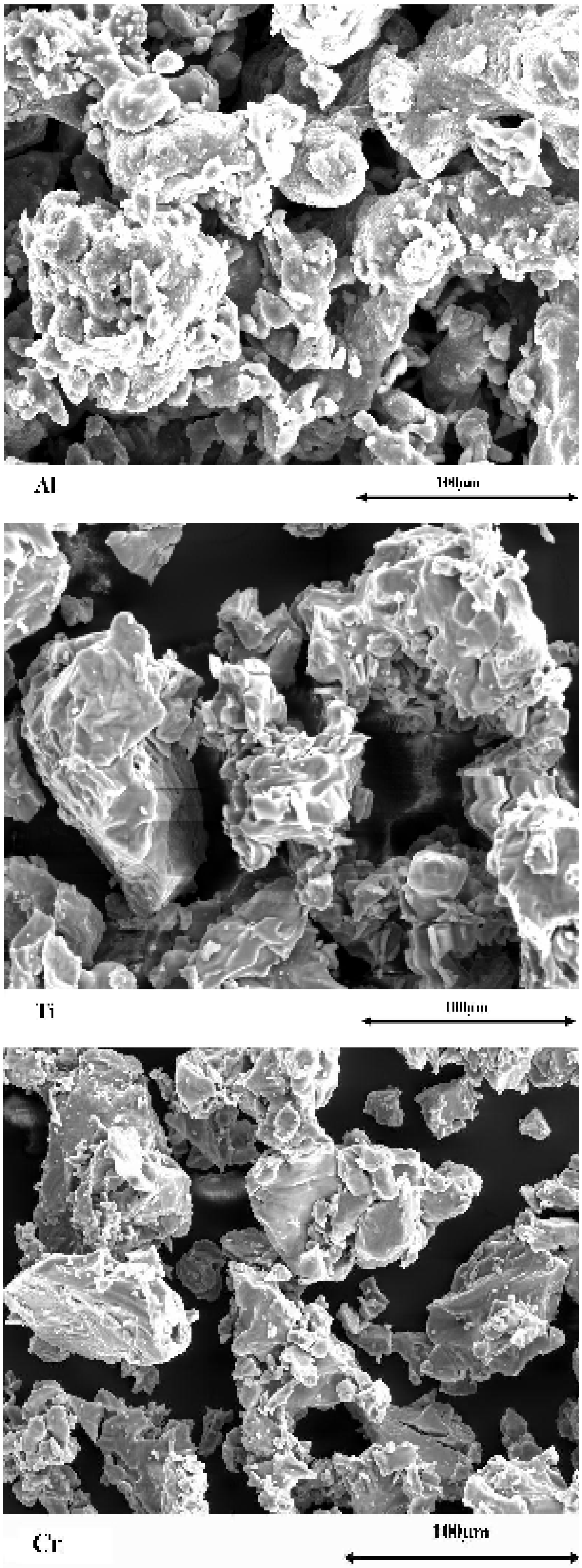

Figure 1. SEM micrographs of elemental powders.

time of alloying process. The lattice parameters of the α-Ti after MA for 10h are approximately a=0.255 nm and c=0.467 nm whereas those before MA are approximately a=0.258 nm and c=0.470 nm so that about 2 % volume shrinkage has occurred, it was due to the diffusion of Al into Ti lattice, which promotes of Ti(Al) solid solution.

After 10 h milling, the powder blend of Ti-50Al transformed to the metastable solid solution of Al in Ti phase and a little metastable solid solution of Ti in Al.

Al is faster diffuser in Ti lattice than that of Ti in Al lattice [21].

The results of XRD patterns showed that the diffraction angles of Ti shifted to higher angles. Considering the smaller size of the Al atom compared with Ti, the lattice parameters and hence the inter-planar spacing, d in the Ti crystal structure is reduced due to the replacement of Al atom for Ti, and therefore the diffraction angle 2θ

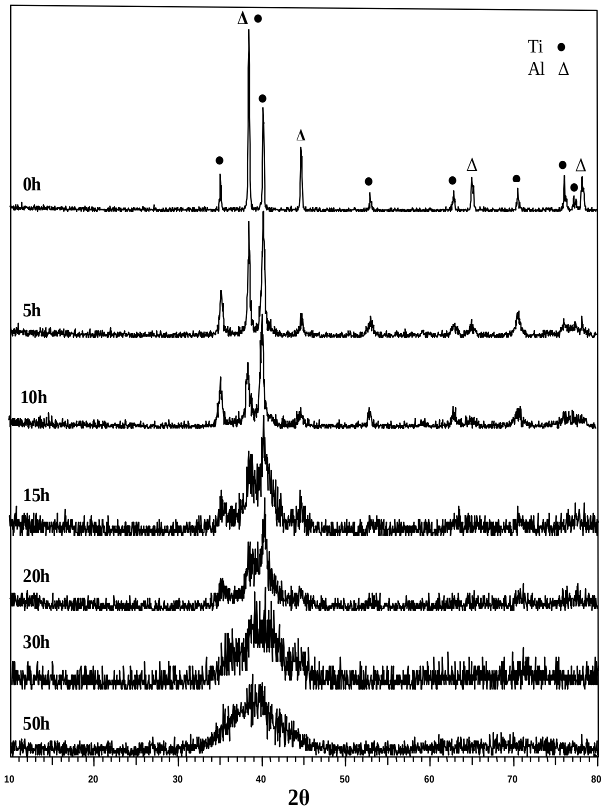

Figure 2. X-ray diffraction patterns of Ti-50Al elemental powder, mechanically alloyed at several alloying times.

is increased according to Bragg's law of 2dsin $\theta=\lambda$, where λ is the X-ray wavelength.

In Figure 3 the study on lattice parameters of elements in powder mixture and shifted angles, showed that after 15 h milling a solid solution of Al and Ti in Cr structure with solid solution of Al in Ti were formed.

Al and Ti have solid solubility in Cr lattice [22]. The Cr solid solution phase did not disappear even after 70 h.

In both cases the diffraction peaks around $2\theta=40^{\circ}$ cannot be separated after 30h milling.

The formation of an amorphous-like phase or very fine particles has been strongly enhanced with increasing the alloying time. Amorphisation 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 [21 and 23]. In Ti-50Al sample, that phase was formed completely after 50h but in samples with 5 at % Cr addition, the Cr(Ti,Al) Solid solution phase together with amorphous phase were remained.

It suggests that Cr(Ti,Al) have weak solubility in powder mixture meanwhile Cr can reduce the amorphisation rate. This might be resulted from lower diffusion rate of Al in Ti in the presence of Cr than those of Cr free powders.

SEM micrographs of Ti-50Al and Ti-45Al-5Cr powders that mechanically alloyed at several alloying times are shown in Figures 4 and 5 respectively.

In both cases, the configuration of each powder turn to a roughly spherical shape and very fine particles after MA process, whereas the starting elemental powders had irregular shapes.

The X-ray mapping images of distribution of elements in sample with 5at% Cr addition showed a homogeneous distribution of Ti, Al and Cr in powder mixture after 50 h (Figure 6) and indicated that not only are the elements of Ti and Al well alloyed to individual particles but the small amount of Cr particles is also dispersed and alloyed into the mechanically alloyed particles.

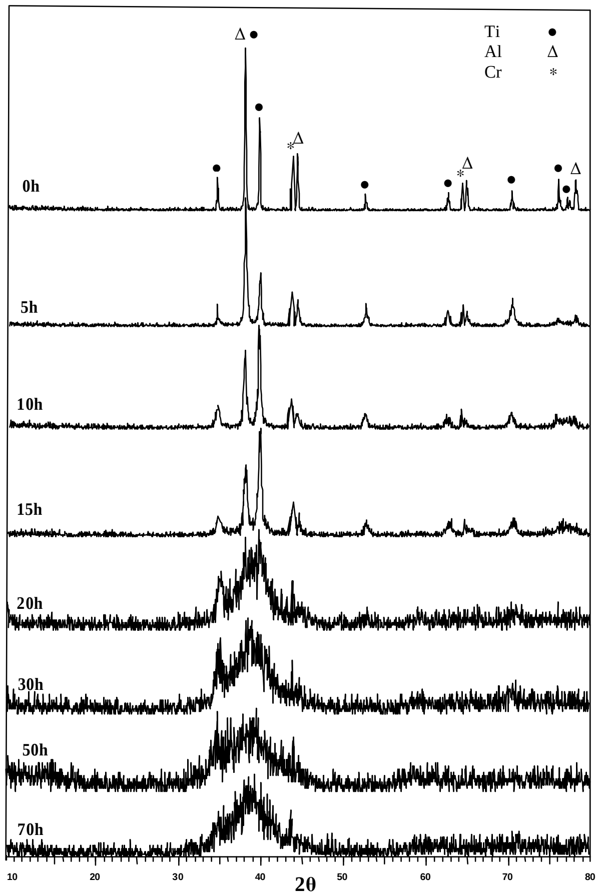

Figure 3. X-ray diffraction patterns of Ti-45Al-5Cr powder, mechanically alloyed at several alloying times.

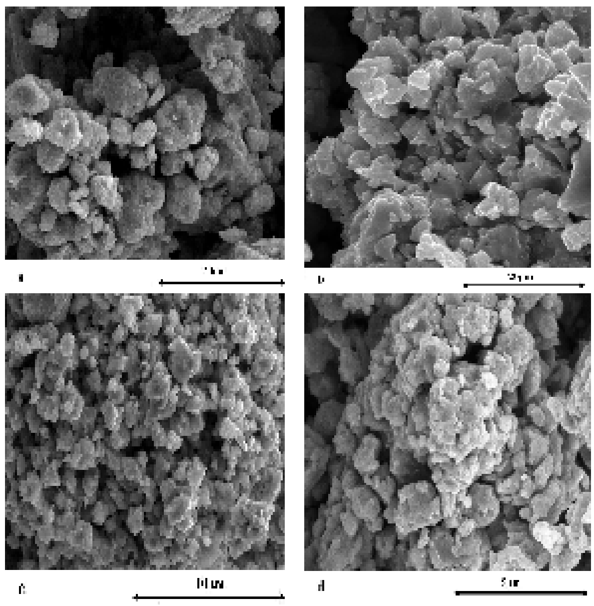

Figure 4. SEM micrographs of Ti-50Al powders mechanically alloyed after (a) 10 h, (b) 20 h, (c) 30 and (d) 50 h.

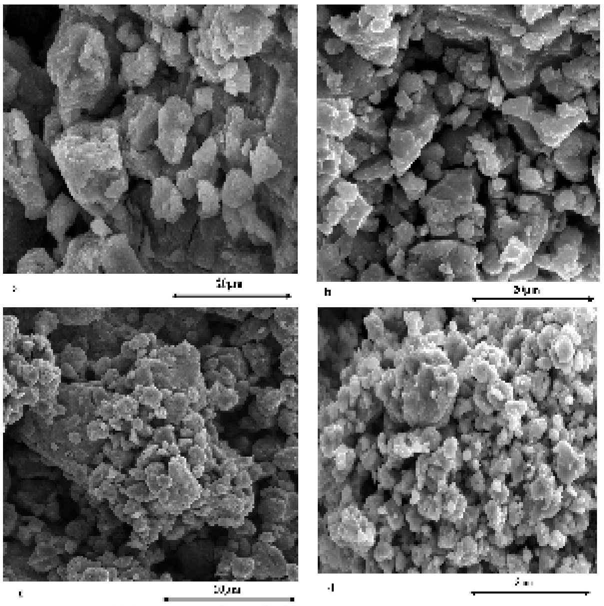

Figure 5. SEM micrographs of Ti-45Al-5Cr powders mechanically alloyed after (a)10h (b)20 h (c)30 and (d)50h.

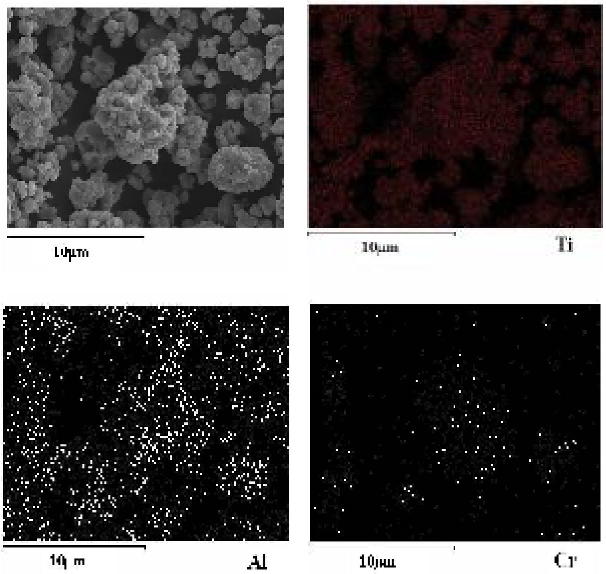

Figure 6. X-ray mapping images of Ti-45Al-5Cr sample after 50 h alloying time.

The grain sizes of productions of MA process were routinely estimated from the XRD spectra with Scherer's analysis (Figure 7).

The grain sizes of particles were decreased with increasing the milling time because the impact energy of the balls which exerted on powder particles increased with increasing the milling time further.

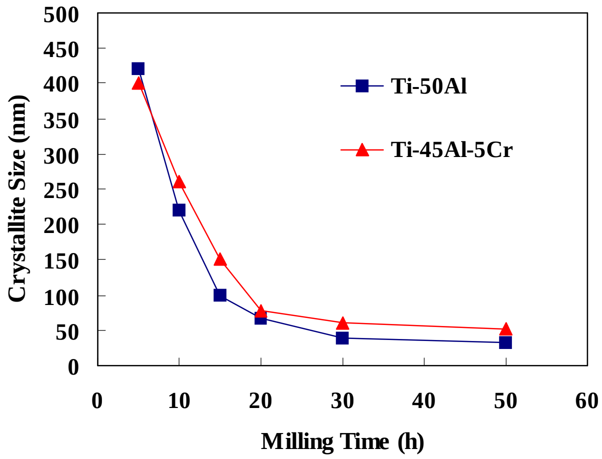

Figure 7. The average grain size of productions of M.A process as a function of alloying time for two samples.

It seems, in samples with 5 at % addition of Cr, the grain sizes of particles are a little larger than Ti-50Al sample.

X-ray diffraction patterns from mechanically alloyed amorphous powders of Ti-50Al and Ti-45Al-5Cr after annealing at 1100ºc in a vacuum furnace for 10 min are shown in Figures 8 and 9 respectively.

These figures indicated a complete phase transformation in mechanically alloyed samples. Both patterns showed that the main phase is the γ-TiAl in both alloys but in Ti-45Al-5Cr, not only the γ-TiAl but also some α_2-Ti_3Al phase was formed. X-ray results indicated that both of the productions had high purity with a very minimum contamination and 40-60nm average grain size.

Addition of 5 % at Cr, shifted the γ-TiAl phase to duplex phase ($\gamma+\alpha_2$) in this system.

In annealed Ti-45Al-5Cr sample, no peaks of Cr or solid solution of Cr compounds was seen in the X-ray diffraction pattern. This indicates the solubility of Cr(Ti,Al) solid solution phase in γ-TiAl and α_2-Ti_3Al.

The result of DTA test on Ti-50Al sample showed an exothermic peak around 450°C. This temperature concern to crystallization of an amorphous TiAl to crystalline γ-TiAl but for Ti-

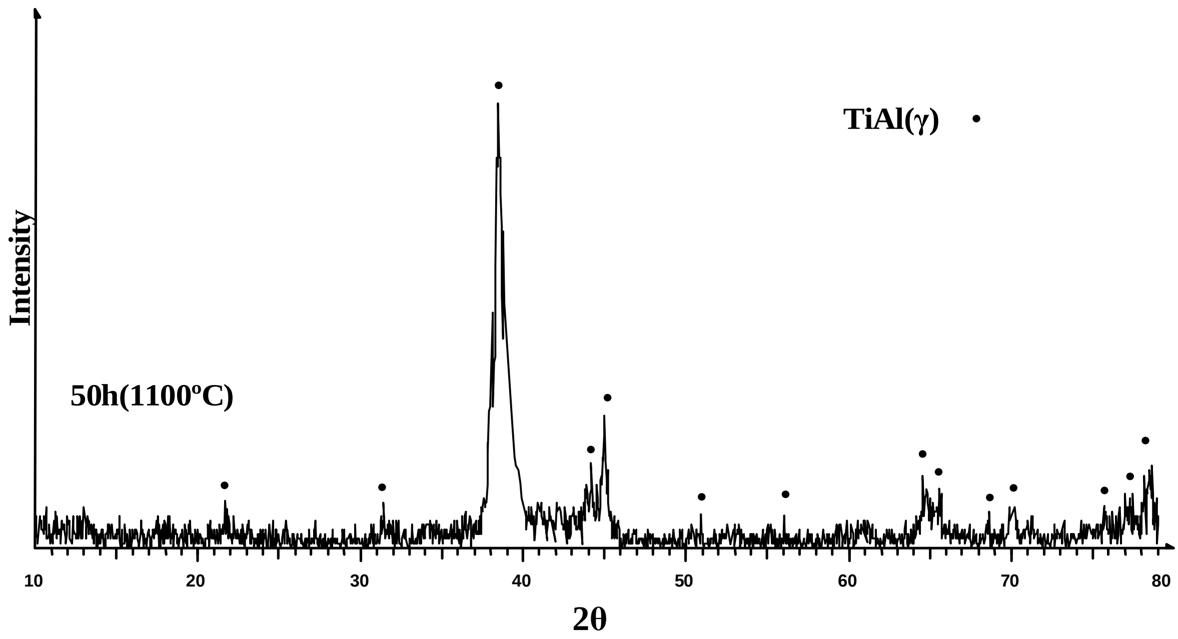

Figure 8. X-ray diffraction pattern of mechanically alloyed Ti-50Al after annealed at 1100˚C for 10min at vacuum furnace.

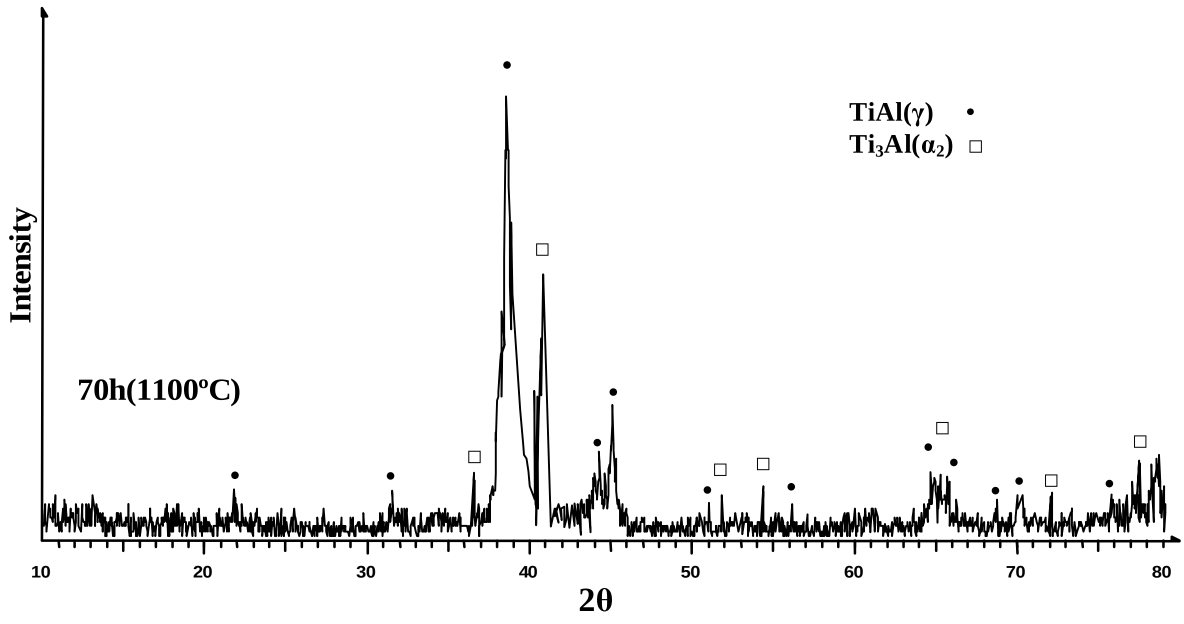

Figure 9. X-ray diffraction pattern of mechanically alloyed Ti-45Al-5Cr after annealed at 1100˚C for 10min at vacuum furnace.

45Al-5Cr sample, results showed two exothermic peaks around 450°C and 570°C which the second peak concern to crystallization of α_2-Ti_3Al phase (Figure 10).

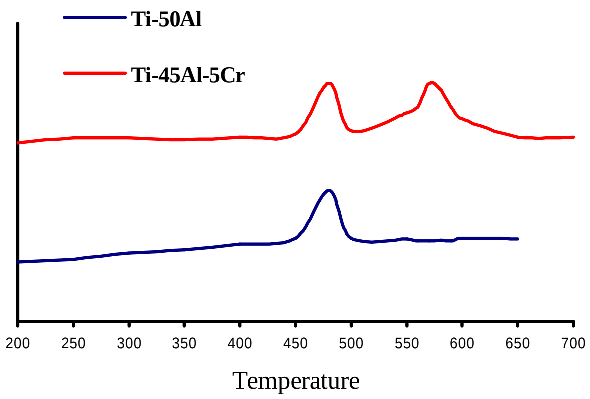

Figure 10. The curve of DTA test for final Ti-50Al and Ti-45Al-5Cr samples.

4. CONCLUSION

During mechanical alloying of Ti-50Al, the Al diffractions disappeared fast that resulted from solution of Al in Ti lattice and formation of metastable solid solution Al in Ti phase.

- After 70 h milling of Ti-45Al-5Cr powder blends, formation of mixture of amorphous phase and Cr(Ti,Al) solid solution phase was observed.
- Addition of 5 % at Cr into TiAl powder mixture decreased the rate of amorphisation.
- After annealing the MAed Ti-50Al sample at 1100°C, the nanostructure TiAl(γ) phase with high purity were produced.
- Addition of 5 % at Cr to the TiAl samples, shifted the γ-TiAl phase to nanostructured duplex phase ($\gamma + \alpha_2$)
- It suggested that Cr(Ti, Al) had solubility in γ-TiAl and α_2-Ti_3Al.

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