Int. J. Nanosci. Nanotechnol., Vol. 8, No. 3, Sep. 2012, pp. 135-142

A Comparison between the Effect of Cr and W Addition on Formation Kinetic of Nanostructure TiAl(γ) Alloy by Mechanical Alloying Route

F. Abbasi Nargesi*, R. Azari Khosroshahi

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

(*) Corresponding author: farshadabbasi60@yahoo.com
(Received:05 Jul. 2012 and Accepted: 28 Aug. 2012)

Abstract:
In this research, mechanical alloying was used to produce Ti-50Al, Ti-45Al-5Cr and Ti-45Al-5W (at%) alloys. The effect of ternary addition (Cr and W) on microstructure and production efficiency of TiAl alloy were investigated. Alloying was performed in a planetary mill and the milling time varying from 5 to 70h. The structural evaluation in these powders was done by X-ray diffraction (XRD) technique and Scanning Electron Microscopy (SEM) during mechanical alloying and after annealing at 1100°C in vacuum oven. The results showed only a complete amorphous phase after 50h of milling of Ti-50Al powder mixture, but with 5at% addition of Cr, the Cr (Ti, Al) solid solution within the amorphous matrix were identified after 70h milling and with 5at% addition of W, the W lattice was remained with amorphous phase. The time required for solid solution or amorphous phase formation was longer in Cr and W containing powders. After annealing of mechanically alloyed Ti-50Al, the γ-phase with high purity and nanostructured size was produced and for sample with Cr addition, the TiAl(γ) with amount of $Ti_3Al(\alpha_2)$ were formed and for sample with W addition, the duplex phase ($\gamma+\alpha_2$) with a minor amount of W, were formed.
Keywords: *Mechanical Alloying, Titanium Aluminide, Chromium, Tungsten, Nanostructure.*

1. INTRODUCTION

In recent years the alloys based on γ-TiAl and α_2-Ti_3Al have received particular attention as a promising structural material for aerospace application. This is essentially due to some attractive properties such as low density, high specific strength and stiffness, high temperature strength retention and creep resistance of these alloys [1-6]. However the poor ductility and fracture toughness at ambient to intermediate temperature are the major obstacles for practical use of these materials. During recent years, many attempts have been made to improve the ductility. Attempts adapted include techniques such as grain refinement to nano-scale structure and microstructure modification [7-9].

Mechanical alloying have been used to refine the grain size and synthesize non-equilibrium structures. Mechanical alloying is described as a high-energy milling process in which powder particles are subjected to repeated cold welding, fracturing and re welding. The transfer of mechanical energy to the powder particles results in introduction of strain into powder through generation of dislocations and other defects which act as fast diffusion paths. Additionally, refinement of particle and grain sizes occurs, and consequently the diffusion distances are reduced [10-12]. This process is a proper method to produce ultra fine grain and nanocrystalline TiAl products [13-15].
Meanwhile, considerable improved ductility and toughness can be achieved in two phase alloys.

Thus, during recent years extensive research has been carried out to develop two phase base alloys consisting of γ-TiAl and α_2-Ti_3Al for application. 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; duplex structure show higher tensile ductility [16-18].
Study the addition of B, Si, W, Cr, Nb, V on MA of TiAl alloys were investigated these years.
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 [19, 20].
The aim of the present work is to study the comparison between the influence of Cr and W addition on the phase structure, microstructure and production efficiency of Ti-Al system during MA and after annealing at 1100°C in vacuum oven.

2. EXPERIMENTAL

Powders of Ti (100-120μm size and 99.8% purity), Al (100-150μm size and 99.7% purity), Cr (60-90μm size and 99.6% purity) and W (80-100μm size and 99.7% purity) were used as starting materials. The powders were initially mixed and weighted to prepare a composition of Ti-50Al, Ti-45Al-5Cr and Ti-45Al-5W (in at %) in a glove box with argon atmosphere. The mechanical alloying process carried out in the FP4 planetary mill with tempered steel and 15, 20mm diameter steel balls. The ball-to-powder weight ratio was 15:1. The rotation speed of the mill was 550rpm. 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. After alloying for various lengths of time up to 70h, the milled powders were withdrawn from the vials for subsequent analysis. The crystal structure of the powders was characterized by a Bruker-D8-Advanced, using Cu-K_α radiation at 30kv and 20mA. 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 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):

$$d = \frac{0.9\lambda}{B\cos\Theta} \quad (1)$$

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

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 of the as milled samples were annealed using an Alcatel CFA-222 vacuum furnace.

3. RESULTS AND DISCUSSION

In order to study the comparison between the effect of Cr and W on kinetic of structural changes during MA process, three compositional Ti-50Al, Ti-45Al-5Cr and Ti-45Al-5W powder blends were mechanically milled for different times.
Comparison of the XRD patterns shown in Figure 1, 2 and 3 indicates that addition of Cr and W to powder blends leads the MA process rates at various stages to be considerably reduced.
In Ti-50Al powder mixture, the diffraction intensities of elements reduced and broadened after 5h alloying and Al diffraction peaks disappeared faster than Ti peaks. The lattice parameters of the α-Ti after MA for 10h are approximately a=0.255nm and c=0.467nm whereas those befor MA are approximately a=0.258nm and c=0.470nm so that about 2% volume shirinkage has occurred, it was due to the diffusion of Al into Ti lattice, which promotes of Ti(Al) solid solution.
Al is diffused faster in Ti lattice in comparison to Ti in Al lattice . After 10h milling, the powder blends of Ti-50Al transformed to metastable solid solution of Al in Ti phase and a little metastable solid solution of Ti in Al [21, 22, 23] .
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 is increased according to Bragg's law of 2dsinθ=λ, where λ is the X-ray wavelength.

In Figure 1, the diffraction peaks around 2θ=40° can not be separated after 30h alloying time.

The formation of an amorphous-like phase or very fine particles has been strongly enhanced with increasing the alloying time [21]. 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 [24]. In Ti-50Al sample, an amorphous phase was completely formed after 50h.

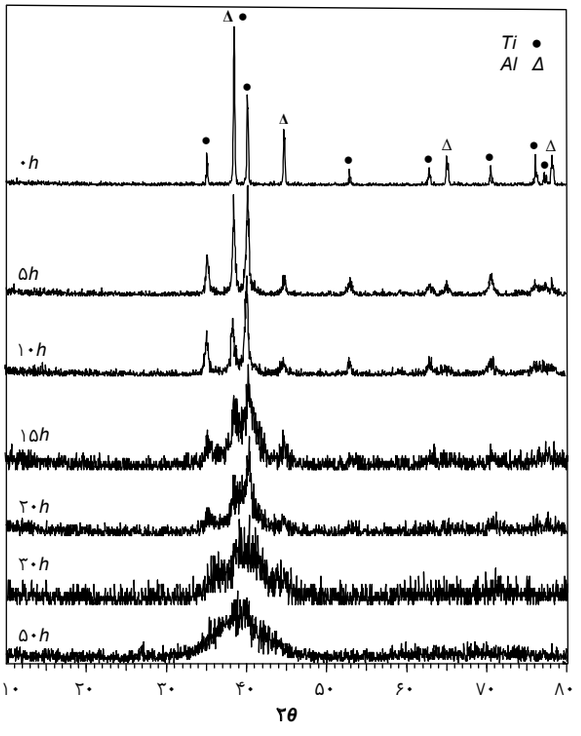

Figure 1: *X-ray diffraction patterns of Ti-50Al powder mixtures at various stages of milling process.*

In Figure 2, the XRD pattern showed that, the diffraction peak of Cr didn't disappear with increasing the milling time.

The study on lattice parameters of elements in powder mixture and the shifted angles showed that after 15h milling a solid solution of Al and Ti in Cr structure and solid solution of Al in Ti were formed. Al and Ti have solid solubility in Cr lattice [25, 26]. An amorphous phase with Cr (Ti, Al) solid solution phase were identified after 70h milling. The same results has been reported by W. Maziraz (2004) and S. Dymek (2006) when they studied mechanical alloying process of various kinds of Ti-Al-Cr powder blends. In samples with W addition, the studies on characterizations of XRD patterns showed that after 15h alloying a minor solid solution of Al in W was formed.

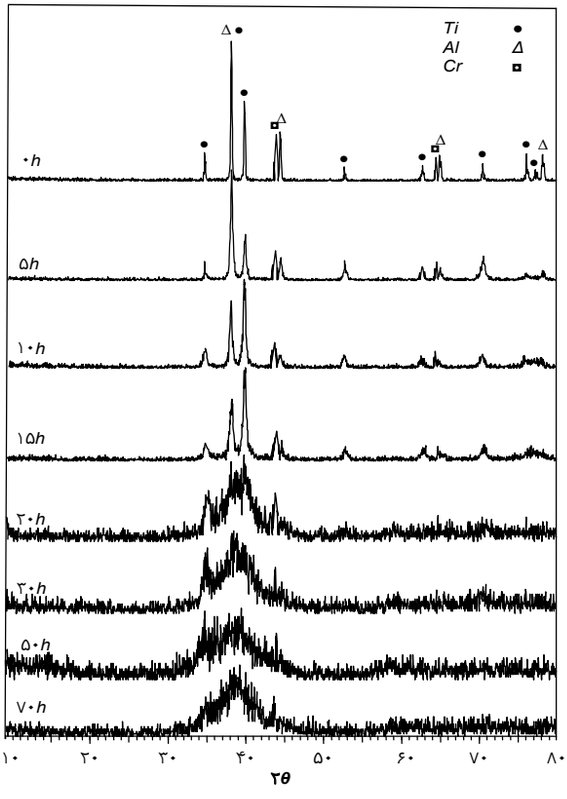

Figure 2: *X-ray diffraction patterns of Ti45Al5Cr powder mixtures at various stages of milling process.*

The solubility of Ti and Al in W is weak. The rate of solid solubility of Al in Ti is larger than Al in W [27, 28]. Comparing Figure 3 with Figure 1, illustrates that W was also decreased the amorphization rate of Ti-Al system.

The final production of mechanical alloyed of Ti-45Al-5W system, was amorphous phase plus W, which appeared after 70h milling.

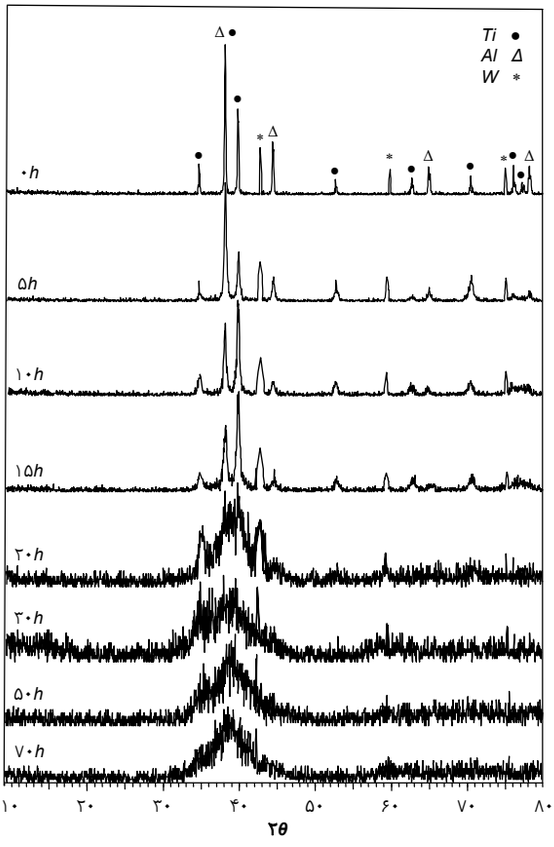

Figure 3: *X-ray diffraction patterns of Ti45Al5W powder mixtures at various stages of milling process.*

SEM micrographs of Ti-50Al, Ti-45Al-5Cr and Ti-45Al-5W powders that mechanically milled at several alloying times are shown in Figures 4, 5 and 6, respectively.

In all cases, the configuration of each powder turns to roughly spherical shape and very fine particles after MA process, whereas the starting elemental powders have irregular shapes.

The grain sizes of productions of MA process were routinely estimated from the XRD spectra with scherrer'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.

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

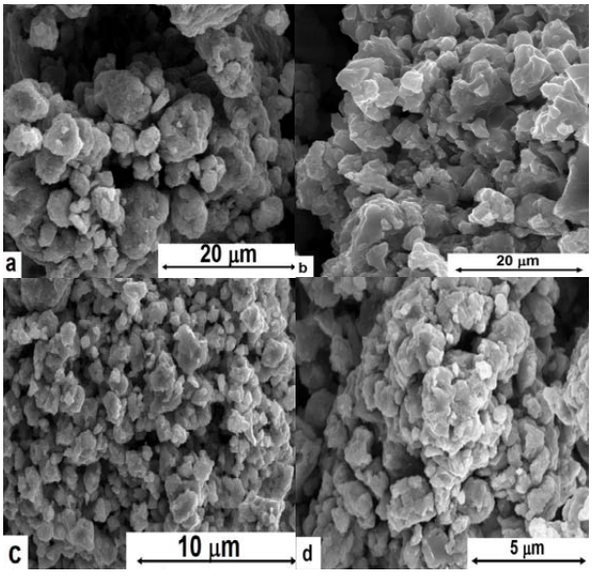

Figure 4: *SEM micrographs of as milled Ti-50Al powder mixtures for (a)10h (b)20h (c)30 and (d)50h .*

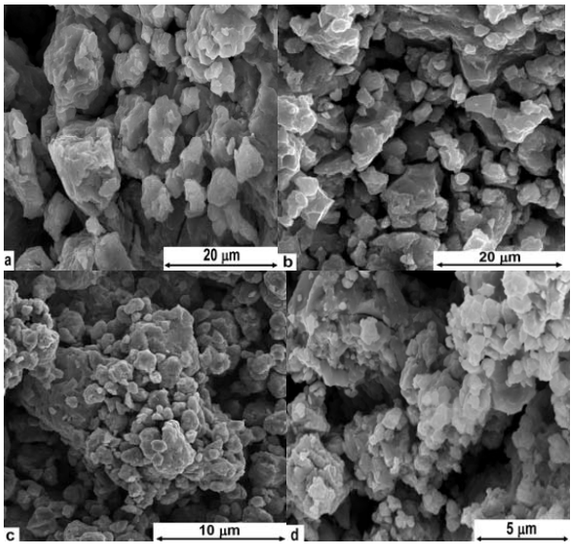

Figure 5: *SEM micrographs of as milled Ti-45Al-5Cr powder mixtures for (a)10h (b)20h (c)30 and (d)70h .*

Figure 8 shows the variation in the amounts of powders recovered from the vial as a function of milling time.

It seems that there is a correlation between sticking tendency of powders mixtures to milling tools and their phase transformation from elemental powder to solid solution phase.

The same observation has been reported by Takasaki, Furya (1999) and Bhattacharya, Bellon (2004) when they studied MA process of various kinds of Ti-Al powder blends.
Figure 8 shows that during structural changes from elemental powder mixtures to Ti solid solution phase, the amount of recoverable powders has been decreased in all samples.

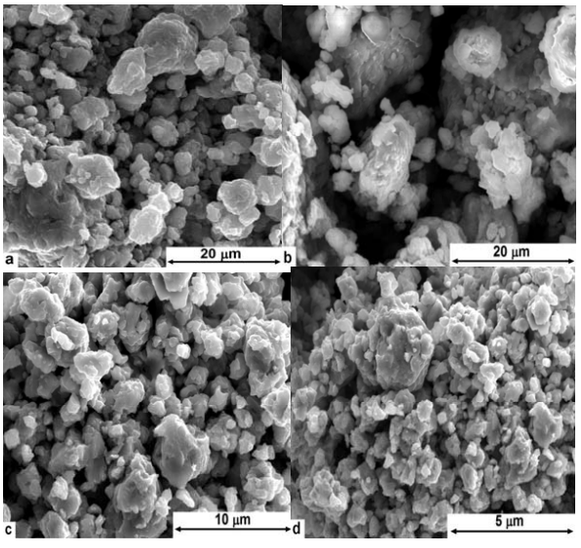

Figure 6: *SEM micrographs of as milled Ti-45Al-5W powder mixtures for (a)10h (b)20h (c)30 and (d)70h .*

In sample with W addition, the recoverable powders seem to be increased with other samples. This might be due to settling of harder W particles between powders and milling tools and preventing from sticking together which results in higher amounts of recoverable powders as compared with two other samples.
X-ray diffraction patterns from mechanically milled amorphous powders of Ti-50Al, Ti-45Al-5Cr and Ti-45Al-5W after annealing at 1100ºC in a vacuum oven for 10 min are shown in Figures 9, 10 and 11 respectively.
The XRD patterns indicated a complete phase transformation in amorphous samples.
The results of XRD patterns showed that the main phase is the γ-TiAl in three productions and the yield have high purity with very minimum contamination. The average grain size of γ-TiAl in productions was 40-70nm. In Ti-50Al annealed sample, only γ-TiAl was detected.
In Ti45Al5Cr annealed sample, γ-TiAl plus α_2-Ti_3Al were formed and we didn't see any Cr or solid solution of Cr compounds in X-ray diffraction pattern. This suggests a solubility of Cr(Ti,Al) solid solution in γ-TiAl and α_2-Ti_3Al.
In sample with W, XRD patterns showed duplex phase (γ-TiAl+α_2-Ti_3Al) with a minor amount of W. Moreover, W demonstrates weaker solubility in γ-TiAl and α_2-Ti_3Al phases.
Addition of 5%at Cr and W, shifted the γ-TiAl phase to duplex phase (γ+α_2) in this system.

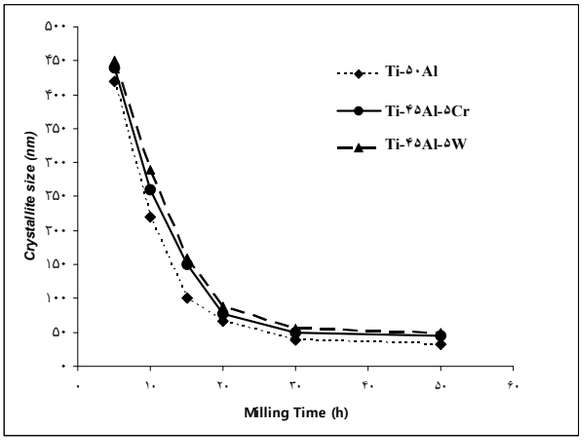

Figure 7: *The average grain size of productions of M.A process as a function of milling time for three samples.*

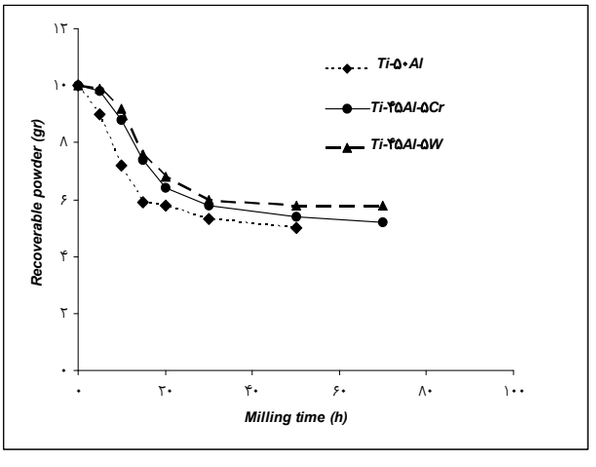

Figure 8: *The amount of recoverable powder products as a function of alloying time.*

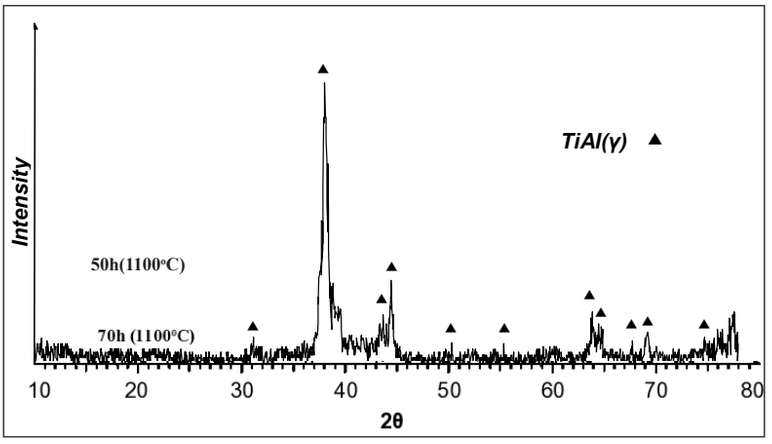

Figure 9: *X-ray diffraction pattern of mechanically milled Ti-50Al powder mixture for 50h after annealing at 1100ºC for 10min.*

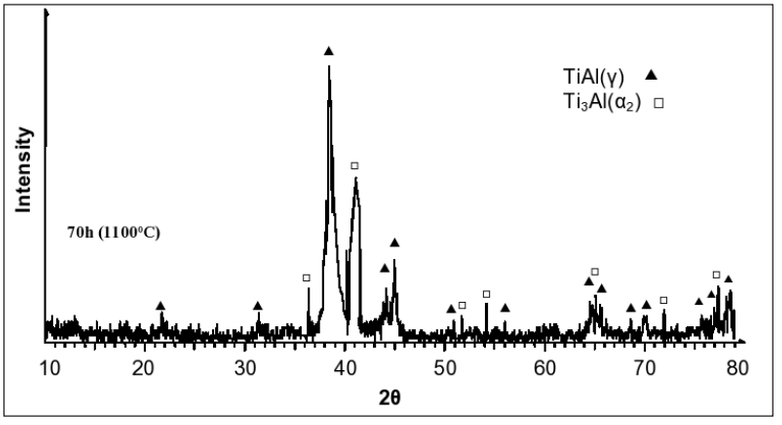

Figure 10: *X-ray diffraction pattern of mechanically milled Ti-45Al-5Cr powder mixture for 70h after annealing at 1100ºC for 10min.*

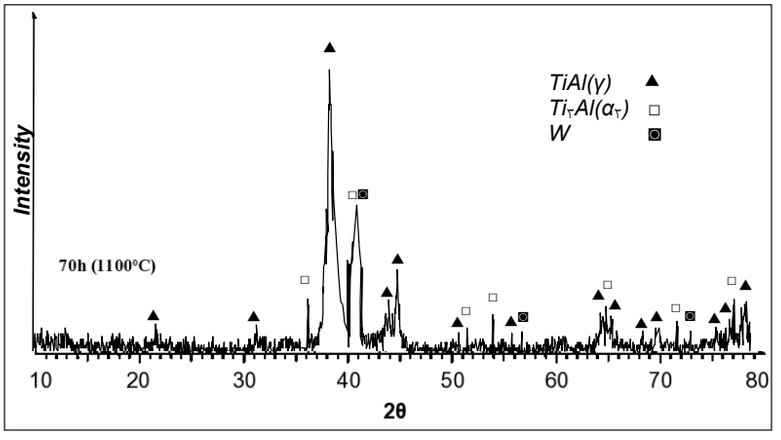

Figure 11: *X-ray diffraction pattern of mechanically milled Ti-45Al-5W powder mixture for 70h after annealing at 1100ºC for 10min.*

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.
- Increasing the milling time accelerated the formation of an amorphous and nano sized mixture.
- After 70h milling of Ti45Al5Cr powder particles, formation of mixture of amorphous and Cr(Ti,Al) solid solution was observed.
- After 70h milling of Ti45Al5W powder particles, formation of mixture of amorphous phase and minor amount of W was detected.
- The time required for amorphous phase formation was longer in Cr and W containing powders compared with Ti-50Al powder mixtures.
- Adhesion tendency of powder mixtures to milling tools was considerably increased during transformation from elemental powder form into solid solution phase. The adhesion tendency of W containing powders was considerably lower than other samples.
- After annealed the MAed Ti-50Al sample at 1100°C, the nanostructure TiAl(γ) phase with high purity were produced.
- Addition of Cr and W to the TiAl samples changed the final phase to nanostructured duplex phase (γ+ α_2).
- The W was remained even after annealing process of amorphous Ti-45Al-5W powder.
- It suggested that Cr(Ti, Al) solid solution had solubility but W had weak solubility in γ-TiAl and α_2-Ti_3Al phases.

REFERENCES

1. T. Kawabata, T. Tamura, O. Izumi, "Effect of TiAl Ratio and Cr, Nb, and Hf additions on Material Factors and Mechanical properties in TiAl", ***Metallurgical TransactionsA***, Vol. 24A, (1993), pp. 141-146.
2. Fanta, G. et al., "Effect of ultrafine grained microstructure on the Hot-Workability of Intermetallic/Ceramic Composites based on γ-TiAl", ***Intermetallics***, Vol. 9, (2001), pp. 45-49.
3. K. R. Cardoso, C. A. D. Rodrigues, "Processing of Aluminium Alloys Containing Titanium addition by Mechanical Alloying" , ***Materials Science and EngineeringA***, Vol. 375, (2004), pp. 1202-1206.
4. K. Uenishi, T. Marsobara, "Nanostructured Titanium-Aluminides and Their Composites Formed by Combustion Synthesis of Mechanically Alloyed Powders", ***Scripta Materialia***, Vol. 44, (2001), pp. 2094-2099.
5. S. H. Kim, H. H. Chung, "Effect of B on the Microstructure and Mechanical Properties of Mechanically Milled TiAl Alloys", ***Metallurgical and Materials TransactionA***, Vol. 20, (1998), pp. 2273-2275.
6. Z. M. Sun, H. Hashimoto, "Fabrication of TiAl alloys by MA-PDS process and mechanical properties", ***Intermetallics***, vol.11, (2003), pp. 826-834.
7. P. Bhattacharya, P. Bellon, R. S. Averback, "Nanocrystalline TiAl Powder Synthesized by High-Energy Ball Milling: Effects of Milling Parameters on Yield and Contamination", ***Journal of Alloys and Compounds***, Vol. 368, (2004), pp. 187-192.
8. A. Takasaki,Y. Furuya, "Mechanical Alloying of The Ti-Al System in Atmosphere of Hydrogen and Argon", ***Nanostructured Materials***, vol.11, (1999), pp. 1209-1217.
9. L. Lu, M. O. Lai and F. H. Froes, "The Mechanical Alloying of Titanium Aluminides", ***JOM***, Vol. 54, (2002), pp. 62-64.
10. M. Sherif El-Eskandarany, "Mechanical Alloying for Fabrication of Advanced Engineering Materials", William Andrew Publication, USA, (2001).
11. C. Suryanarayana, "Recent Developments in Mechanical Alloying", ***Rev. Adv. Mater. Sci.*** , Vol. 18, (2008), pp. 203-211.
12. 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), pp. 612-623.
13. K. B. Gerasimov, S. V. Pavlov, "Metastable Ti-Al Phases Obtained by Mechanical Alloying", ***Journal of Alloys and Compounds***, Vol. 242, (1996), pp. 136-140.
14. 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), pp. 115-119.

15. H. Huang, P. Virtanen, T. Tiainen, "Synthesis of γ-TiAl Based Alloy by Mechanical Alloying and Reactive Hot Isostatic Pressing", ***Journal of Materials Engineering and Performance***, Vol. 7, (1998), pp. 784-788.

16. E. Hamzah, M. Kanniah, "Microstructure and Creep behaviour of as-cast Ti-48Al-4Cr", ***Modern Applied Science***, Vol. 3, (2009), pp. 164-168.

17. H. S. Park, S. K. Hwang, "Microstructural Refinement and Mechanical Properties Improvement of Elemental Powder Metallurgy Processed Ti-46.6Al-1.4Mn-2Mo Alloy by Carbon Addition", ***Metallurgical and Materials Transactions A***, Vol. 23A, (2001), pp. 251-258.

18. E. Paransky, E. Y. Gutmanas, I. Gotman and M. Koczak, "Pressure Assisted Reactive Synthesis Of Titanium Aluminides From Dense 50Al-50Ti Elemental Powder Blends", ***Metallurgical and Materials Transaction A***, Vol. 27, (1996), pp. 2130-2136.

19. S. Dymek, M. Wrobel, "Effect of 5at% Addition of Cr, V and W on Microstructure and Mechanical Properties of γ-TiAl Based Alloys", ***Archives of Metallurgy and Materials***, Vol. 5, (2006), pp. 97-101.

20. Dong-Bok Lee, "Effect of Cr, Nb, Mn, V, W and Si on High Temperature Oxidation of TiAl Alloys", ***Metals and Materials International***, Vol. 11, (2005), pp. 141-148.

21. L. Lu, M. O. Lai, "Mechanical Alloying", Kluwer Academic Publishers, Boston, (1998).

22. F. Abbasi Nargesi, R. Azari Khosroshahi, N. Parvini Ahmadi, "The Influence of Process Control Agent's State on Expedition of Mechanical Alloying of Nanostructure TiAl(γ) Alloy***", IJE Transactions B: Applications***, Vol. 23, No. 2, (2010), pp. 139-145.

23. F. Abbasi Nargesi, R. Azari Khosroshahi, N. Parvini Ahmadi, "Studing The Effect of Productive Factors on Synthesis of Nanostructure TiAl(γ) Alloy by Mechanical Alloying***", IJE Transactions B: Applications***, Vol. 23, No. 2, (2010), pp. 147-156.

24. C. Suryanarayana, "Mechanical Alloying and Milling", ***Progress in Materials Science***, Vol. 46, (2001), pp. 100-140.

25. W. Maziarz, A. Michalski, "Structure and Mechanicall Properties of Ball Milled Ti-Al-Cr Intermetallics Consolidated by Hot Pressing and Pulse Plasma Sintering", ***Rev. Adv. Mater. Sci***. , Vol. 8, (2004), pp. 158-163.

26. F. Abbasi Nargesi, R. Azari Khosroshahi, N. Parvini Ahmadi, "Synthesis of Nanostructure Ti-45Al-5Cr Alloy by Mechanical Alloying and Study the Effect of Cr Addition on Microstructure of TiAl Alloy***", IJE Transactions A: Basics,*** Vol. 24, No. 2, (2011), pp. 123-130.

27. S. Dymek, M. Wrobel, M. Blicharski, "Influence of Tungsten Microstructure of Mechanically Alloyed γ-TiAl", ***Journal of Microscopy***, Vol. 223, (2006), pp. 292-294.

28. O. Yiafang, Zh. Xiaping, "Extended Solid Solubility for Al-W binary System by Mechanical Alloying", ***Science in China(Series A)***, Vol. 43, (2000), pp. 180-184.