Phase stability of mechanically alloyed Ti-Fe-Al alloys

IOP Conf. Series: Materials Science and Engineering **973** (2020) 012025 doi:10.1088/1757-899X/973/1/012025

Phase stability of mechanically alloyed Ti-Fe-Al alloys

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Abstract Iron alloying element addition to pure titanium can be used to enhance strengthening as well as β-phase stabilizer. However, the outcome depends on the processing route to some extent. Mechanical alloy technique is adapted in this work to produce titanium alloys with 7wt% iron content and 1wt% Aluminum. The obtained nano-size particles have two phases α and β structures and the formation of the second β-phase is mainly enhanced by the milling force. Heating the produced grain compacted powder to a temperature above the beta phase transus temperature followed by quenching to ambient temperature resulted in α-martensite partial transformation. This result can indicate that the obtained β-phase for the present alloys is not fully stabilized by the iron additions.

1. Introduction

The Ti-6Al-4V (in wt.%) is one of the most widely used alloys for aircraft high performance automobiles and biomedical prosthesis. This alloy has a dual phase microstructure α and β at room temperature [1]. The aluminum addition to this Ti-base alloy is intended to stabilize the hcp α-phase and increase the strength whiles the vanadium to introduce a second β-phase to the microstructure and enhance both ductility and toughness. However, for medical applications vanadium is cytotoxic and it′s also an expensive element [2-6]. Also, titanium alloys such as Ti-6Al-7Nb, Ti-5Al-2.5Fe and Ti-6Al-4V still contained Al which has been suggested to cause osteolysis and neural disorders such as Alzheimer′s disease [7, 8].

Recently Ti-based alloys with up to 7wt.% Al and a small addition of Fe that doesn′t exceed the 2wt.%have been developed with the aim of reducing the cost and maintaining mechanical properties and biocompatibility to a level close to Ti-6Al-4V alloy[9]. Substitution of vanadium in Ti-6Al-4V with iron and niobium did not significantly affect the electrochemical behavior[10]. The amount of formed β-phase in the microstructure relative to α phase depends not only on alloy composition but also on the processing conditions and subsequent treatment. Furthermore, the volume fraction of β phase has been reported to increase with strain during superplastic deformation, where stress induced transformation take place[11]. The deformation behavior of β-Ti alloys is shown to be strongly dependent on the degree of the β-phase stability [12]. The deformation mechanism changes from slip deformation to deformation twinning and/or martensitic transformation with decreasing the β phase stability. The stress-induced martensitic transformation β→α″(orthorhombic) is not stabilizing alloying elements dependent but also stress level can have a determining role [13].

2. Material and techniques

Ti-Fe-Al alloys were prepared from the constituent elements Ti, Fe, and Al with purity grades higher than 99.9%. In the mechanical alloying process, the required mixture and hardened stainless steel balls were loaded together into a water-cooled stainless steel pot under argon atmosphere at speed of 500 rpm with 1:20 powder to ball ratio. The process was stopped almost each one hour to keep the milling temperature close to room temperature. The green compacted mechanically alloyed powder particles have been solution treated at 950 and 1100°C under argon atmosphere and followed by water quenching to examine structure thermal stability and sintering tendency.

XRD analysis was performed using a Siemens D5000 powder diffractometer equipped with Cu Ka radiation (wavelength = 0.15406 nm) with a nickel filter at 40 kV and 30 mA. Thermal analysis was performed in the temperature range from 25 to 1100°C using a AT instrument SDT Q600, with heating rate 10 K/min. The microstructure features of the samples have been investigated using a Field-Emission Scanning Electron Microscopy Quanta FEG 250and Transmission Electron Microscopy JEOL TEM-2100. Sample composition was analyzed by energy dispersive X-ray spectroscopy (EDX).

3. Results and discussion

Mechanical alloying is a solid-state powder processing technique involving repeated welding, fracturing, and rewelding of powder particles. In this process, the mixture of microcrystalline pure Ti, Fe, and Al elements, with alloy composition of Ti-7Fe-1Al weight percent were milled as a function of mechanical alloying time up to 12 hours. The typical XRD pattern of the mixture before and after milling time is shown in figure 1. The original shape lines of all elements gradually became broader and their intensity decreases with milling time. The partial formation of Fe and Al solid solution in the α-Ti matrix can be deduced from such decreases in intensity of X-ray peaks for both Fe and Al. Since the powder particles are subjected to severe plastic deformation, high density of defects generated and subsequently a distortion in the formed solid solution crystal structure are to be expected.

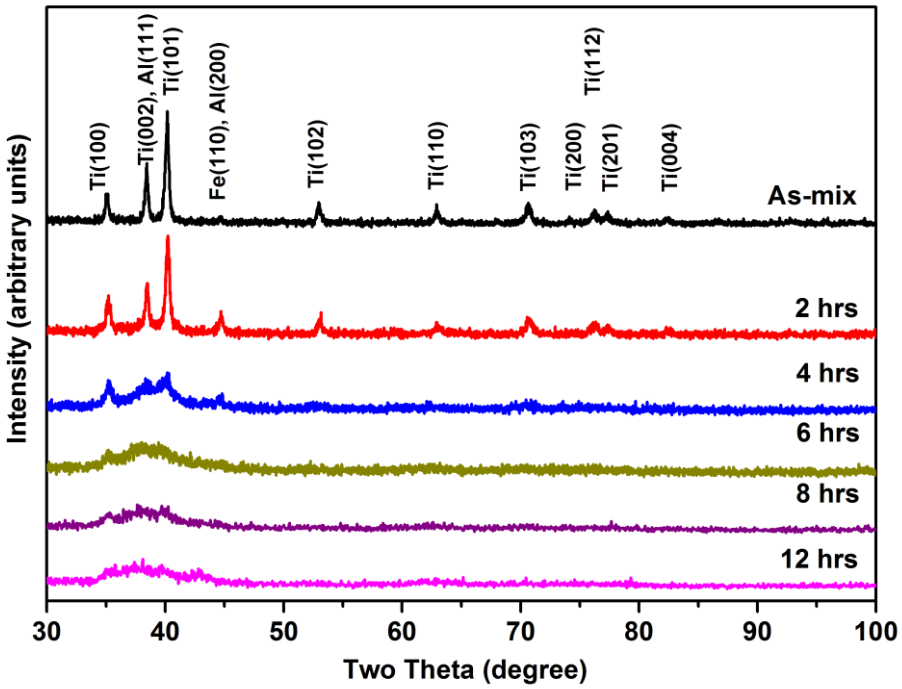

Figure 1. XRD patterns of Ti-7Fe-1Al up to 12 hours of ball milling.

The original XRD patterns contains mainly the α-Ti phase which completely matched with the JCPDS-ICDD standard cards number (44-1294), in additions to two small in intensity peaks for both

Al (65-2869) and/or Fe (01-1267). After 4 hours of milling, these two extra lines from Fe and Al disappear which can be attributed to the deformation process, the refining of the microstructure and/or to the possible formation of a supersaturated solid solution in the α-Ti matrix. Peak broadening continues with milling time representing the refinement in the particles structure and an increase of the internal strain. The line (101) of alpha phase has been shifted to lower angle values with milling time and resulted in differences in $\Delta d = 0.0442$nm decrease after 4h milling. This might suggest an interface orientation relation between α and β-phase mainly α-(101) and β-(110).

During milling process, both iron and aluminum penetrate in Ti simultaneously leading to increases in Fe/Al concentration ratio in newly formed phase as suggested by the different elements mapping for their distribution, figure 2. The Al-element appears almost homogeneously distributed in the whole area, figure 2b, however iron distribution seems to be high concentrated in the lighter zone of the iron map, figure 2d, the higher iron concentration zone corresponding to the β-phase and a rough estimation of the volume fraction of this phase particles to be around ≈ 10% at this stage of milling. Therefore, such observation confirms the β-phase presence in addition to α-phase matrix. This also suggested that the nano-particles β-phase originated from the supersaturated Al/Fe solid solution in titanium.

The degree of crystallinity to amorphization formed in the structure can only be conformed using TEM investigation. TEM analysis of mechanically alloyed powder indicated the presences of nano-crystalline phase. As shown in figure 3, the diffraction pattern indicates the presence of randomly oriented nano-crystal. The pattern also consists of rings sampling all possible planes. Further, the micrographs confirmed the nano-particles microstructure and the spot arranged in circles suggests the presence of high angle-boundaries in ultra-fine structure. The diffuse characteristic of the spots is a strong indication of the lattice distortion associated with milling stress. The destabilization of the crystalline phase is thought to occur during mechanical alloying by increasing the free energy due to the accumulation of structural defects such as vacancies, dislocations, and grain boundaries. The continuous refinement in grain size is therefore increasing the boundaries area and lattice expansion could also contribute to increasing the free energy of the deformed phase.

A differential thermal analysis DTA test was carried out for Ti-7Fe-1Al mechanically alloyed powder sample in a range of temperatures up to 1100°C, as shown in figure 4. Two exothermic peaks are observed at 120 and 325°C. Both peaks could be attributed to annealing the high concentration of defects, associated with the milling process. Further heating to a relatively higher temperature resulted in the formation of an endothermic peak at ≈ 786°C which can be associated with the possible allotropic transformation of α→β phase change. Such a transformation is generally known to occur at 882°C for pure Ti and the decrease of this transition temperature is mainly due to the presence of alloying elements, Fe and Al and additional reduction could be due to the small powder particle size used for the test compared to the bulk compacted specimen. Since the starting powder for the thermal test is mainly composed of α+β phases, therefore the amount of β is expected to increase with heating and a fully single β phase would be reached passing the 786°C temperature.

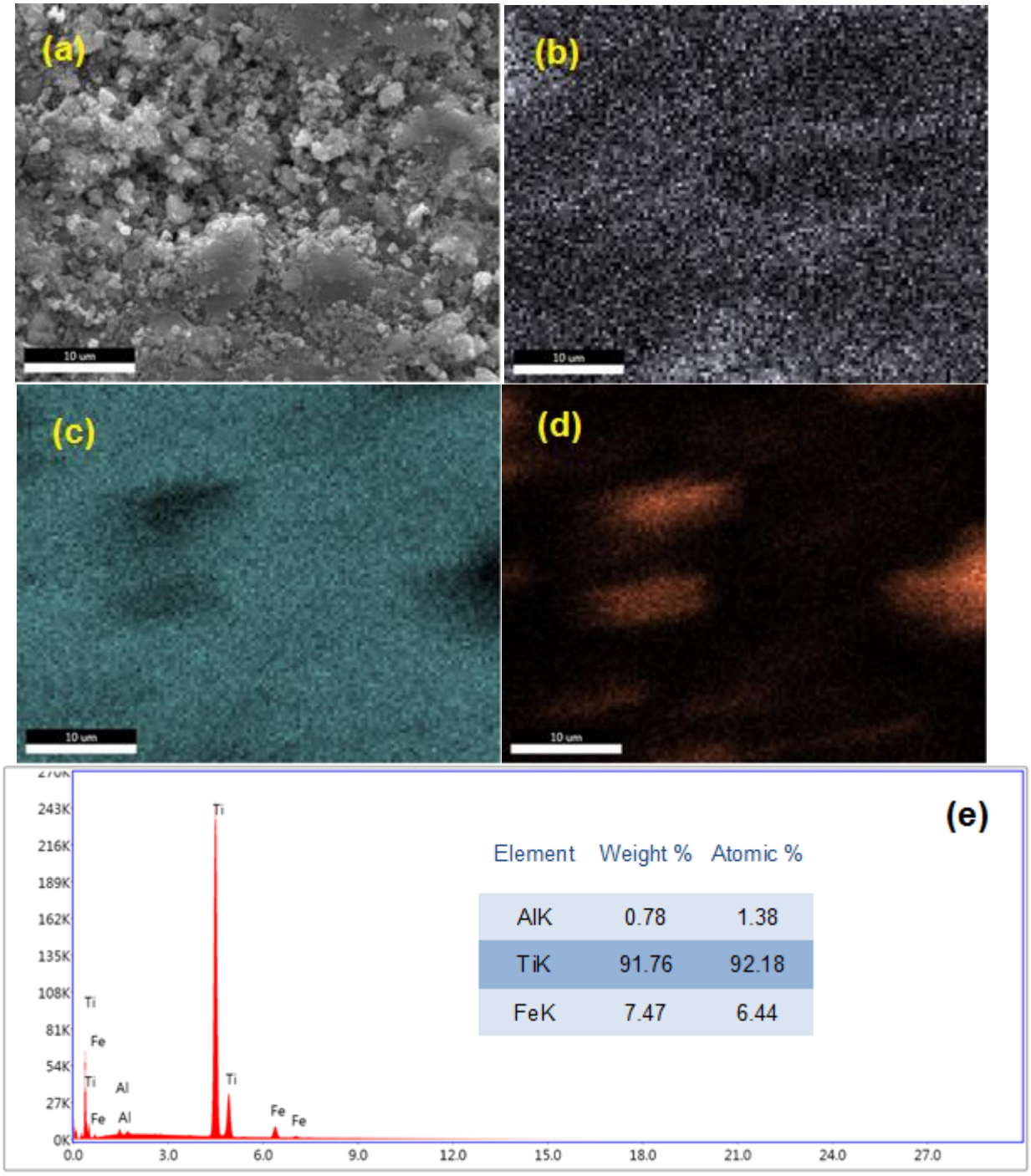

Figure 2. (a) SEM image of the as-milled sample Ti–7Fe–1Al alloy and its X–ray element distribution maps: (b) Al, (c) Ti, (d) Fe and (e) EDX

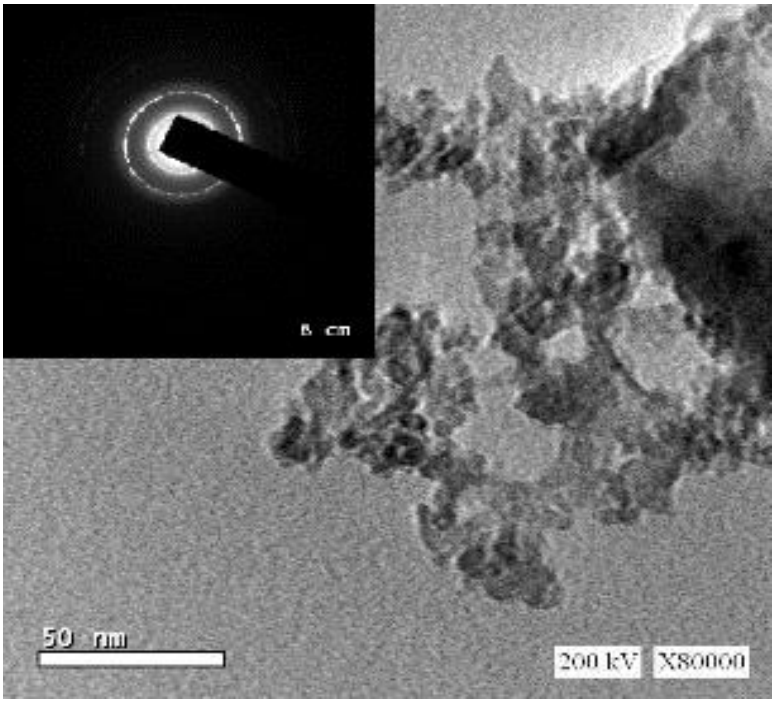

Figure 3. TEM micrographs of Ti-7Fe-1Al after 6 hours of ball milling.

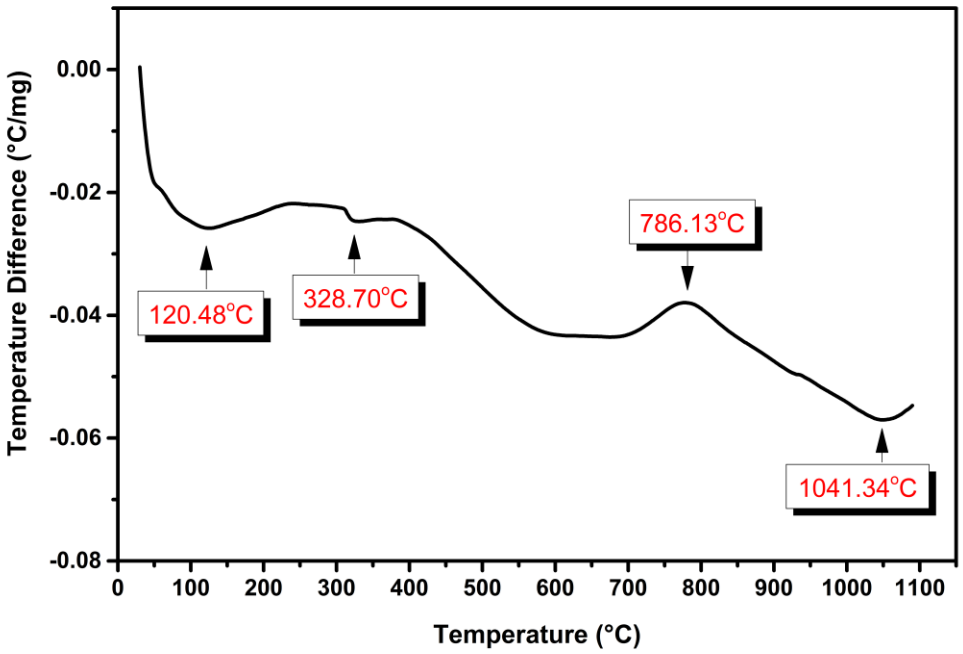

Figure 4. DTA curve for Ti-7Fe-1Al mechanically alloyed powder sample.

In the binary equilibrium diagram for Ti-Fe [14, 15], a temperature of ≈ 826°C for fully β-phase with 7wt.%Fe, which is 40°C more than the measured one, indicates a possible enhancement of α→β transformation by stored energy during milling. In that case, the Fe lean α phase loses its iron content to further stabilize the high temperature β-phase. High temperature binary Ti-Fe system shows a eutectic reaction at 1085°C in the Ti side of the diagram, similar exothermic presuming due to the

eutectic reaction but occurs at slightly lower temperature of 1041°C. On the other hand, there is another eutectoid reaction at 595°C of β→α+TiFe, but no trace of such reaction is observed on the thermal diagram. The suppression of the eutectoid reaction and consequently the formation of the intermetallic TiFe phase has been reported by several works assuming kinetic reasoning for such changes [16].

The α-Ti phase is known to have low symmetry (hcp) structure which lack sufficient independent slip system when compared to Ti-β phase with (bcc) symmetry. The amount of newly formed β-phase in the present ternary system at early stage of milling will continue to generate a high rate of dislocation during milling. The formed dislocations are not expected to pass through the α-phase and accumulate at the interface between α/β phases, creating a large stress concentration at the interface resulting in a stress gradient from the interface to α-grain interior. Such condition can enhance the diffusion flow mainly for the fast diffusion element Fe. The iron migration from the interface to the interior of α phase, will enrich α phase with iron atoms with the subsequent effect of increasing the structure instability and compel α phase to transform to β-phase. This transformation starts at the interface and gradually extends to grain interior with strain. Further, the high stress concentration formed at the interface will significantly increase the Gibb′s free energy in addition to the enrichment by Fe atoms will eventually cause a high order of lattice instability of the α phase near the interface. Transformation from α to β phase to reduce the rise in free energy will occur gradually and depend on both Fe diffusivity and the amount of strain produced at the interface. Similar trend of result has been observed with Ti-Al-Fe alloy but at lower iron content [11, 17]. Thermal stability of the pre-milled alloys was examined at of 950 and 1100°C for different holding times. X-ray diffraction patterns indicated that, the 950°C quenched samples transformed to α′-Ti phase. The intensity of the peaks corresponding to α′ phase decreases for the 4hrs milled sample while 6 hrs milled sample quenched from 950 shows α′ and α″-Ti phases formation. Also, the 1100°C quenched sample indicate that, the α″-martensitic phase is the dominate structure.

The microstructures of the Ti–7Fe-1Al without milling shows α′-martensite phases formation. According to XRD results, increasing milling time leads to the significant increasing in the amount of α″-phase after quenching, hence β phase mostly not found. The quantity of α′ phase is decreased with milling time. The length of the longest martensitic plates was about 30.6 μm. Only primary and secondary martensite plates are visible in figure 6. Figures 7 and 8 show SEM image of the quenched samples from 950 and 1100°C, a nano size particle appeared to dominate the microstructure in addition to porosity. SEM observation indicated that the times for isothermal holding up to two hours at both selected temperatures were not enough for the green compacted particles to rich a complete densification microstructure. The porosities in the obtained microstructures are observed to decreases with both times and temperatures of the thermal treatment and they are mainly located along the particles boundaries and some appears interconnected with irregular shape as shown in figure 6. It therefore possible to suggests that the thermal energy during this early stage of particles sintering is mainly spent in the alloying elements diffusion for α + β → β transformation, rather the compact densification. The diffusivity and solubility limit of alloying elements in the high temperature β-phase which dictate the kinetic of densification process. As previously indicated the iron has a high diffusivity in titanium and mainly in β-phase which will enhance the alloys sinterability. On the other hand, this high diffusivity of iron can be responsible for the formation of Kirkendall porosities the titanium matrix.

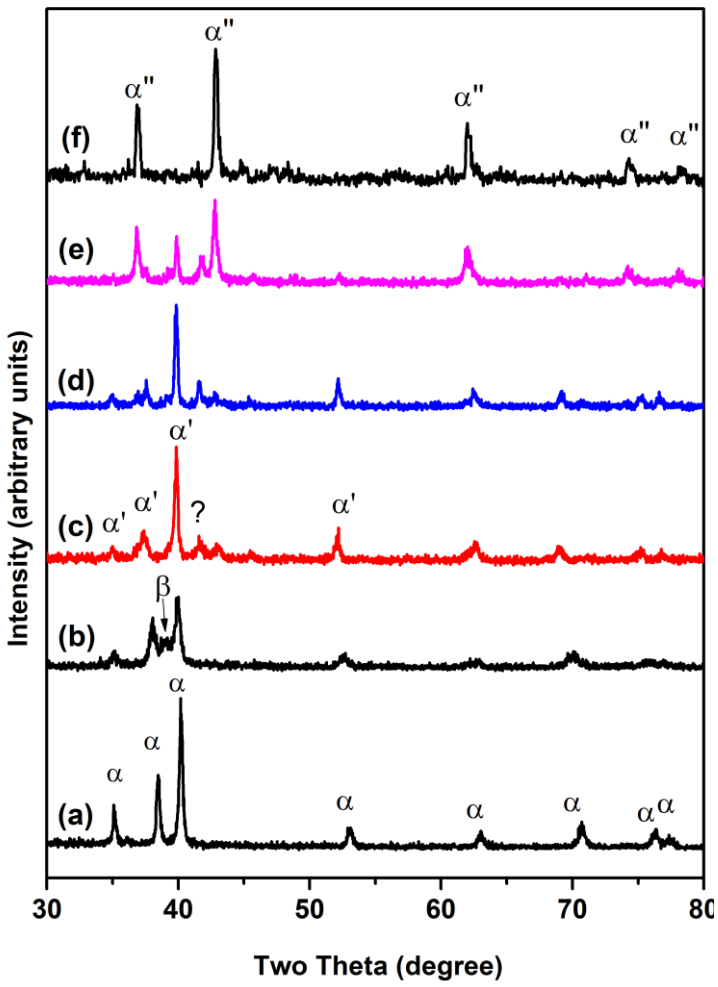

Figure 5. XRD patterns of as-quenched Ti-7Fe-1Al from 950°C (b) without milling, (c) 2 hrs, (d) 4 hrs and (e) 6hrs, and from 1100°C (f) 6hrs, compared with initial α-Ti (a)

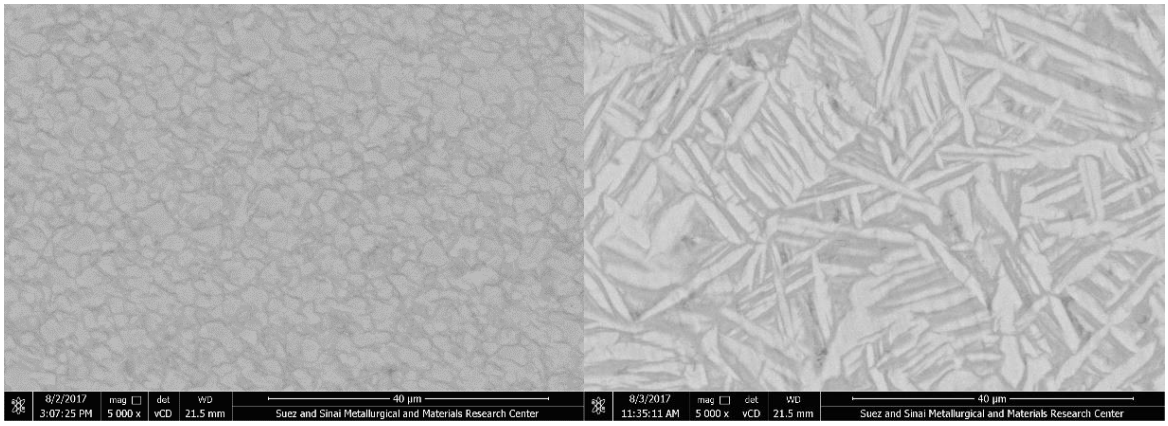

Figure 6. SEM of Ti-7Fe-1Al without milling quenched from 950°C.

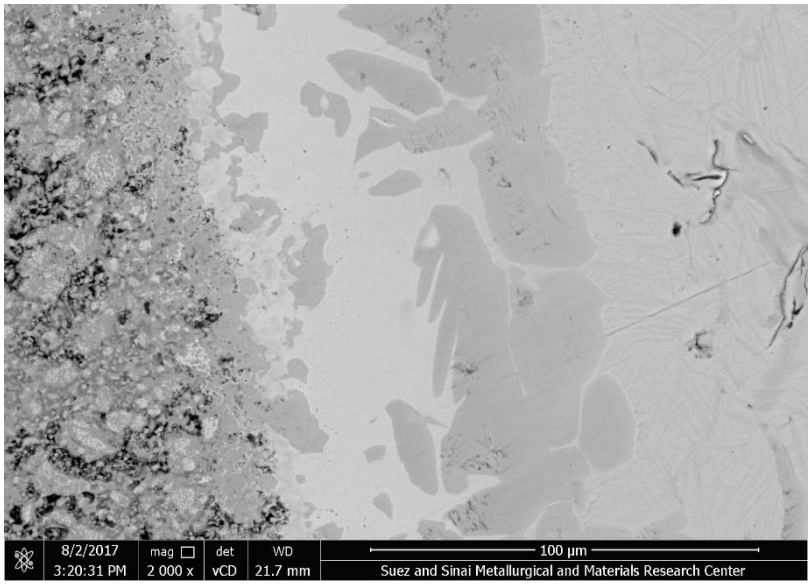

Figure 7. SEM of 4hrs milled sample Ti-7Fe-1Al quenched from 950°C**.**

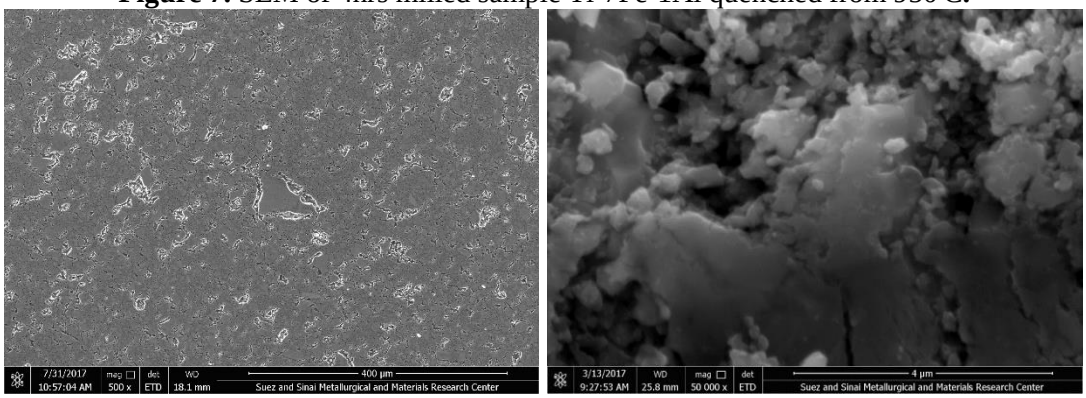

Figure 8. SEM of 6 hours milled Ti-7Fe-1Al quenched from 1100°C.

A volume contraction is observed following the solution treatment indicating the start of densification process however it is not completed due to the relatively short isothermal holding times; between 1 and 2 hours before quenching. In this process of the solid solution above β transition temperature the primary effect will be to enrich the β-matrix with β-stabilizing elements, mainly Fe. The high residual strain produced by the previous milling process is expected to enhance densification for nano particles of the compacted powder in addition to accelerating any expected diffusion process of particle growth. Moreover, at the higher solution treatment temperature of 1100°C, the presence of Fe will lead to the formation of a eutectic reaction at 1085°C leading to an increase in the alloy sinterability due to the transient liquid phase formation. Furthermore, the diffusivity of Fe in β-Ti is known to be higher than that in α-Ti and can lead to a fast decomposition of α-phase and the formation of the single β-phase above T_β. The presence of Al in the alloy composition is not likely to contribute to improvement of sintered density since it has been suggested that a partial Ti-Al diffusion can lead to a residual pore formation. On the other hand, Al-addition has been shown to act as β-stabilizing elements, but only with single β-Ti phase [18].

XRD results of different solution treated samples at 1100°C showed that the quenching to room temperature produced a β→α″ martensitic transformation. However, the intensities of α″-lines are less strong at higher Fe content alloys with a few lines of β and even α-phase. This could be an indication that the higher Fe-content is more stable than the lower one and therefore, the metastable β-structure with lower Fe-content is expected to give more martensitic transformation. Similar results were

obtained after specimens treated at 950°C, however it appears that a different quenching rate has a considerable effect on martensitic volume fractions. In that respect, the change in quenching rate is expected to create a change in the degree of solute partitioning during cooling.

The phase stability indicators parameter calculated for present alloy composition and shown in table1 predicted the formation of the β-stable and/or near β-phase to occur during processing. Since the fully β-stability is associated with retarding the displasive phases at room temperature by quenching. The absence of such results is considered as discrepancies to experimental and calculated parameters. Such discrepancies can be attributed with a possible shift of the boundary between the phases with ternary content of alloying elements. Moreover, the additive effect of each alloying element on titanium may need to be reconsidered and replaced by interactive form between trio-elements electronic structures. It has been generally indicated that the finer the parent phase grain size, martensite will form easier and would be thus in a more stable condition. Also, refinement of grain size could lead to an increase in the transformation temperatures and in a more general term, the effect of the stored energy due to milling process will reduce the temperature for recovery, recrystallization and grain growth.

4. Conclusions

The milling of the titanium base alloys showed a nanosize double phase α and β with particles size been iron content dependent. The accumulated stored energy during milling is partially enhancing the second β-phase formation in the α-matrix. TEM observation of milled powder confirm the presence of a nanocrystalline microstructure with high angle boundaries. The thermal stability of the pre-milled particles in a grain compacted form undergoes a martensite type of transformation α-phase with orthorhombic structure following the quenching from a temperature above the beta-transus temperature. Such transformation is considered as an indication that a full β-stable phase is not reached with the present iron content in titanium base alloy but rather a β metastable phase is obtained.

References

[1] Wang Q, Liu Z, Wang B, Hassan Mohsan AU. 2017. *Materials Science and Engineering: A* 690: 32-6
[2] Wang K. 1996. *Materials Science and Engineering: A* **213** pp 134-7
[3] He G, Eckert J, Dai QL, Sui ML, Löser W, et al. 2003. *Biomaterials* **24** pp 5115-20
[4] Xie KY, Wang Y, Zhao Y, Chang L, Wang G, et al. 2013. *Materials Science and Engineering: C* **33** pp 3530-6
[5] Song Y, Xu DS, Yang R, Li D, Wu WT, Guo ZX. 1999. *Materials Science and Engineering A* 260: 269-74
[6] Yang YF, Luo SD, Schaffer GB, Qian M. 2012. *Metallurgical and Materials Transactions A* **43** pp 4896-906
[7] Perl DP. 1985. *Environmental health perspectives* **63** pp 149-53
[8] Kiss T. 1995. *Archives of Gerontology and Geriatrics* **21 pp** 99-112
[9] Fujii H. 1998. *Materials Science and Engineering: A* **243** pp 103-8
[10] Choubey A, Basu B, Balasubramaniam R. 2005. *Trends Biomater. Artif. Organs, Vol 18 (2), January* **18** pp 64-72
[11] Koike J, Shimoyama Y, Ohnuma I, Okamura T, Kainuma R, et al. 2000. *Acta Materialia* **48** pp 2059-69
[12] Xu W, Kim KB, Das J, Calin M, Eckert J. 2006. *Scripta Materialia* **54** pp 1943-8
[13] Jackson M, Ahmed W. 2007. In *Surface Engineered Surgical Tools and Medical Devices*, pp 533-76(Boston, MA: Springer US)
[14] Ozaki T, Matsumoto H, Watanabe S, Hanada S. 2004. *Materials Transactions* **45** pp 2776-9
[15] Neelakantan S, Rivera-Díaz-del-Castillo PEJ, van der Zwaag S. 2009. *Scripta Materialia* **60** pp 611-4
[16] Moiseev VN. 1969. *Metal Science and Heat Treatment* **11** pp 335-9

[17] Kilmametov A, Ivanisenko Y, Straumal B, Mazilkin AA, Gornakova AS, et al. 2017. *Scripta Materialia* **136** pp 46-9
[18] Abdel-Hady M, Hinoshita K, Morinaga M. 2006. *Scripta Materialia* **55** pp 477-80