PREPARATION AND CHARACTERIZATION OF Ti-12Mo/x Al_2O_3 NANO-COMPOSITES FOR AEROSPACE APPLICATIONS

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ABSTRACT
Titanium powder is reinforced with 12 wt. % molybdenum powder, and then the mixed Ti-12%Mo matrix composite powder is reinforced with 5, 10, and 15 wt. % nano Al_2O_3 by the mechanical milling for 24 hr. The mixed nano-composite powders were cold compacted under 600MPa, then sintered at 1450°C for 90 min. The microstructure and chemical composition of the Ti-12Mo/Al_2O_3 powders, as well as the fabricated composites, were investigated by both SEM and X-ray diffraction. It has been observed form the SEM studies of the sintered samples that the Al_2O_3 and Mo particles were homogeneously distributed all over the Ti matrix. All the composites were evaluated by measuring their density, hardness, and wear resistance. The results revealed that the addition of 12 wt. % Mo to pure titanium improves its density due to its high density over than that of the Ti and the good adhesion between them, while the addition of Al_2O_3 decreases the density of the Ti-12Mo nano-composite. Not only the density of the Ti was improved by the addition of Mo, but also the hardness and wear resistance were also increased. Regardless of the decreasing in the density of Ti-12Mo nano-composite by increasing the Al_2O_3 wt. %, the hardness and wear resistance were improved up to 5 wt. % Al_2O_3.

Keywords: Powder Metallurgy; Titanium Matrix Nano-Composites; Hardness; Wear Rate; Aerospace Applications.

1. INTRODUCTION
Aerospace systems and performance-enhancing automobiles involve materials with enhanced features such as high strength, resistance to temperature, wear resistance, ductility, the toughness of fracture, fatigue resistance, etc. It must be as high as possible while minimizing other parameters such as density and cost; the latter is of general concern for automotive applications and relatively cheap light aircraft [1, 2]. Titanium alloys are used in aircraft, armor plating, naval vessels, spacecraft, and rockets due to their high tensile strength to density ratio, high corrosion resistance, high crack resistance, and capacity to resist moderately elevated temperatures without creeping [3, 4]. Titanium alloyed with aluminum, vanadium and other elements are used for these apps for a multitude of components including critical structural parts, firewalls, landing gear, exhaust ducts (helicopters) and hydraulic systems. In reality, about two-thirds of all titanium metal generated is used in motors and frames for aircraft. Titanium alloys have to be considered a much younger structural material compared to steels or aluminum alloys. In the United States, the first alloys were created in the late 1940s. Among these was the Ti-6Al-4V classic titanium alloy, which still captures a big proportion of today's aerospace applications [5, 6]. High specific strength and great corrosion resistance are the outstanding characteristics of titanium alloys. Titanium alloys are therefore discovered in aerospace applications where the combination of

weight, strength, corrosion resistance and/or high-temperature stability of aluminum alloys, high-resistance steels or super alloys based on nickel is insufficient [7].

Pure elements do not have properties that make it able to resist forces and chemical attacks so that they need to integrate with other elements to balance their physical and mechanical properties. Composite materials are materials fabricate with two or more constituent materials with different physical or chemical properties. Combining more one element produces a material with different characteristics from each individual component. Powder metallurgy technique is the best method for producing composite materials with homogeneous properties [8-10]. There are several types of particles, whiskers or fibers ceramics that can be used as reinforcement in composites (as SiC, Al_2O_3, TiC, WC and diamond) according to the required application of the materials. Ceramic reinforced particle metal matrix composites (PMMC) have many mechanical advantages over the metal matrix. Generally, PMMC's have higher strength, hardness, strength to weight ratio and in some cases have higher strength at elevated temperatures. This improved the economical aspect of the product since manufacturing is possible with conventional tooling. Therefore, it is important to investigate the mechanical and metallurgical properties of such composites, specifically wear behavior. Alumina has high hardness, good stability, high oxidation capacity, very low friction coefficient (high wear resistance), and low bending stress [11–13]. Addition of alumina with other materials, from metals, intermetallics or ceramics, forming composite materials can improve alumina's mechanical properties [14, 15].

The primary objective of this research is replacing vanadium with molybdenum as a beta stabilizer material and studying the effect of sintering temperature on the densification of the prepared composites. Also, investigation of the effect of alumina nanoparticles content on the density, chemical composition, composites microstructure, hardness, and wear rate of the fabricated composites.

2. EXPERIMENTAL METHODS AND PROCEDURES

2.1. Materials

As received, titanium powder with 99.8% purity and 45µm particle size (Tohotec Inc.), molybdenum powder of 100 µm particle size (dop. turkey), and aluminum oxide powder of 200 nm particle size (Zircar Co. LTD) are used as a raw materials to prepare a Ti matrix composite suitable for dental applications. Different mixtures contain 12 wt. % Mo and 88 wt. % Ti as a matrix reinforced with 0, 5, 10, and 15 wt. % Al_2O_3, are prepared by mechanical milling for 24 hr. 2 wt. % of ethanol is added as a process controlling agent. The milling process is achieved in the argon atmosphere; protect Ti composite from any oxidation during the milling process. The milling conditions are 100 rpm speed by using 10 mm balls diameter. The ratio ball to powder is 10:1. The milled mixtures were dried at 60°C for 30 minutes to get rid of ethanol. The X-Ray diffraction and Scanning Electron Microscopy (SEM) are used to estimate the chemical composition and morphology of the introduced powders as well as the fabricated composites.

The prepared Ti-12Mo/x (Al_2O_3) composites mixtures of powders are cold compacted under 600 MPa by a uniaxial press in a die with dimensions17 x12 mm^2. The thickness of the pressed samples was 6mm. To determine the suitable sintering temperature of the composites, they are heated at 1300°C, 1350°C, 1450°C, and 1500°C for 90 min soaking time. Figure 1 shows the heating cycle of the sintering process. The 1450°C was the best sintering temperature for the composites.

In order to prepare the composites for the microstructure evaluation, samples are ground using 400, 800, 1500, 2000, and 4000 grade SiC papers, respectively, then polished using a diamond paste of 3 μm particle size. An extensive microstructural and morphological study is performed to investigate Ti, Mo, Al_2O_3 powders and Ti-12Mo/Al_2O_3 mixtures, as well as for the Ti-12Mo/Al_2O_3 sintered samples by QUANTA FEG250-EDAX Genesis scanning electron microscope. The chemical composition and phase analysis of both powders, and sintered materials are investigated by the X-ray diffraction (XRD) of the model D8 kristalloflex.

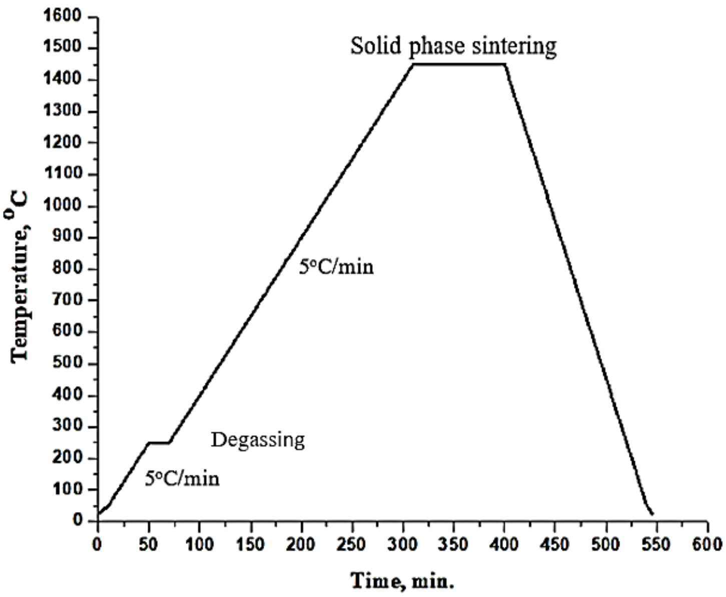

Fig. 1: Heating cycle of the sintering process.

2.2. Physical Properties Measurements

The densities of the bulk materials are determined by Archimedes method according to the following equation using the water as a floating liquid, as shown in the following equation [16].

$$\rho_{Arch.} = \frac{w_{air}}{(w_{air} - w_{water})} \quad \text{...} \quad (1)$$

Where, W_{air} and W_{water} represent the specimen weight in air and water, respectively.

2.3. Mechanical Properties Investigation

Vickers hardness of Ti-12Mo/Al_2O_3 sintered composites are measured using Vickers hardness tester of the model (Matsuzawa JAPAN) by applying 20 kg load and 15 sec loading time at room temperature. The test is repeated for each specimen five times at different regions along the specimen cross-section, and the average of them is recorded as the value of the sample hardness.

The wear test is carried out by the laboratory pin-on-ring method. The pin-on-ring adhesive wear test involves applying high stress between two abrasion bodies, wherein this test a rectangular pin specimen is fixed against a rotating hardened stainless steel ring. Prior to testing, the samples and ring were ultrasonically cleaned and washed in acetone. The wear behavior is studied by determining the weight loss, where specimens are weighed before and after applying the test using a scale with a sensitivity of 0.0001 gm. Each reported wear value is the average result obtained from two separate measurements.

3. Results and Discussion

3.1. Powder Characterization

The morphology of titanium, molybdenum, nano-alumina, and the milled Ti-12Mo/15 wt. % Al_2O_3 nano-composite powders are shown in figure 2 (a, b, c and d), respectively. It is clear from SEM that the size of the powders are in the range from 2-5 µm. Different shapes of particles are detected, the first is the irregular shape for Ti, the rod-like shape for Mo particles, and a flakey for the Al_2O_3. As a result of continuous mechanical milling for 24 hr., the particle size composite mixture is reduced to a nano-scale, less than 100 nm as shown in figure 2 (d).

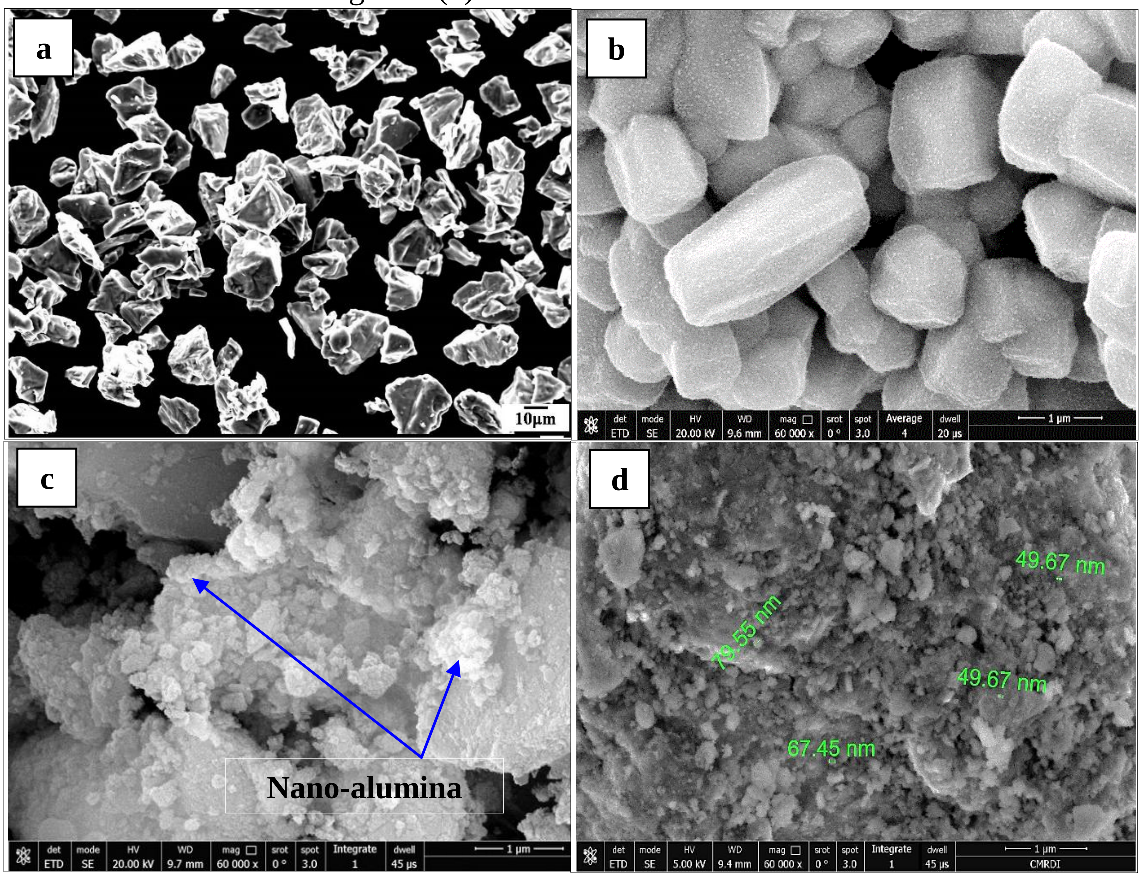

Fig. 2: SEM of the as received powders (a) Titanium, (b) Molybdenum, (c) Nano-alumina, and (d) 15 wt. % Al_2O_3 powder composite.

3.2. Sintered Composites Characterizations

3.2.1. Density measurement

The relative density of the Ti-12Mo/x Al_2O_3 nano-composites is the percentage of the sintered density of the composites to their theoretical density of the mixed powders. Figure 3 shows the effect of reinforcing Ti matrix with 12Mo and different percentages of Al_2O_3 up to 15 wt. % on the relative density. It was observed that Ti-12Mo without any alumina achieved relatively higher densities of 99.4 %. The density of Ti-12Mo was decreased by increasing the amount of Al_2O_3. For instance, 5 wt % Ti-12Mo/ Al_2O_3 was found to be 98.9 pct dense and it decreased slightly to 97.8 % for 10 wt % Ti-12Mo/Al_2O_3 and to 97.2 for 15 wt % Ti-12Mo/Al_2O_3. Decreasing the density of the Ti-12Mo nano-composite matrix with increasing the Al_2O_3, may be due to more than one reason that summarizes in the lower density of the Al_2O_3 than that of Ti-12Mo matrix, and poor wettability of Al_2O_3 as a ceramic material with both Ti and Mo, which increases the chance for pore formation on the interface between Al_2O_3 particles and Ti matrix, that decreases the densification.

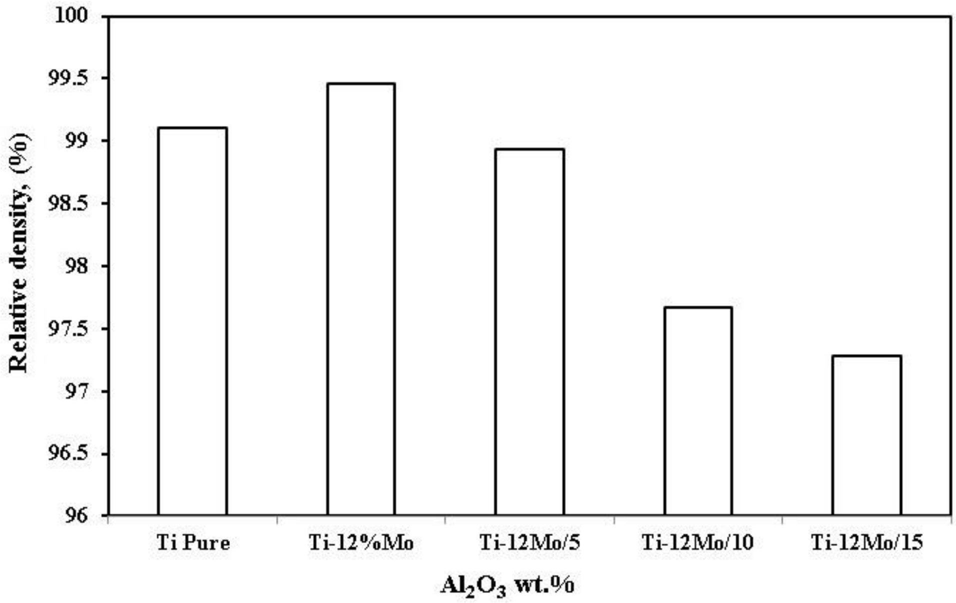

Fig. 3: Effect of Al_2O_3 percent on Ti-12Mo composite density.

3.2.2. X-Ray Diffraction Analysis

The purity of the used raw materials, which are Ti, Mo, and Al_2O_3 powders, are checked by the XRD analysis. As shown in figure 4 (a), no phases rather than Ti, Mo, and Al_2O_3 are detected, which prove that the used raw materials have high purity. Besides detecting of purity of the received raw materials, their crystal structures were evaluated. The analysis emphasizes that the Ti has Hcp crystal structure, Mo has a BCC, and Al_2O_3 has a rhombohedral crystal structure.

On the other hand, to detect the interaction between the different elements after the mixing process for 24 hr., and during the sintering process, the composite materials also checked by the XRD analysis. Figure 4 (b) shows the XRD patterns of the mixtures (Ti-

12Mo, and Ti-12Mo/15 wt. % Al_2O_3) and the fabricated Ti-12Mo/15 wt. % Al_2O_3. As shown in figure 4 (b) no any new chemical compositions are detected after the mixing and sintering processes. Owing to the milling and sintering in an inert atmosphere.

The Peak broadening gives an indication of the particle size, where the wider the diffraction peak, the smaller the particle size [17]. Comparing the width of the peaks of the pure elements, and the composites after milling and sintering, it can be seen that the peaks broadening after milling and sintering are wider than the peak broadening of the used materials, which means decreasing the particles size after milling.

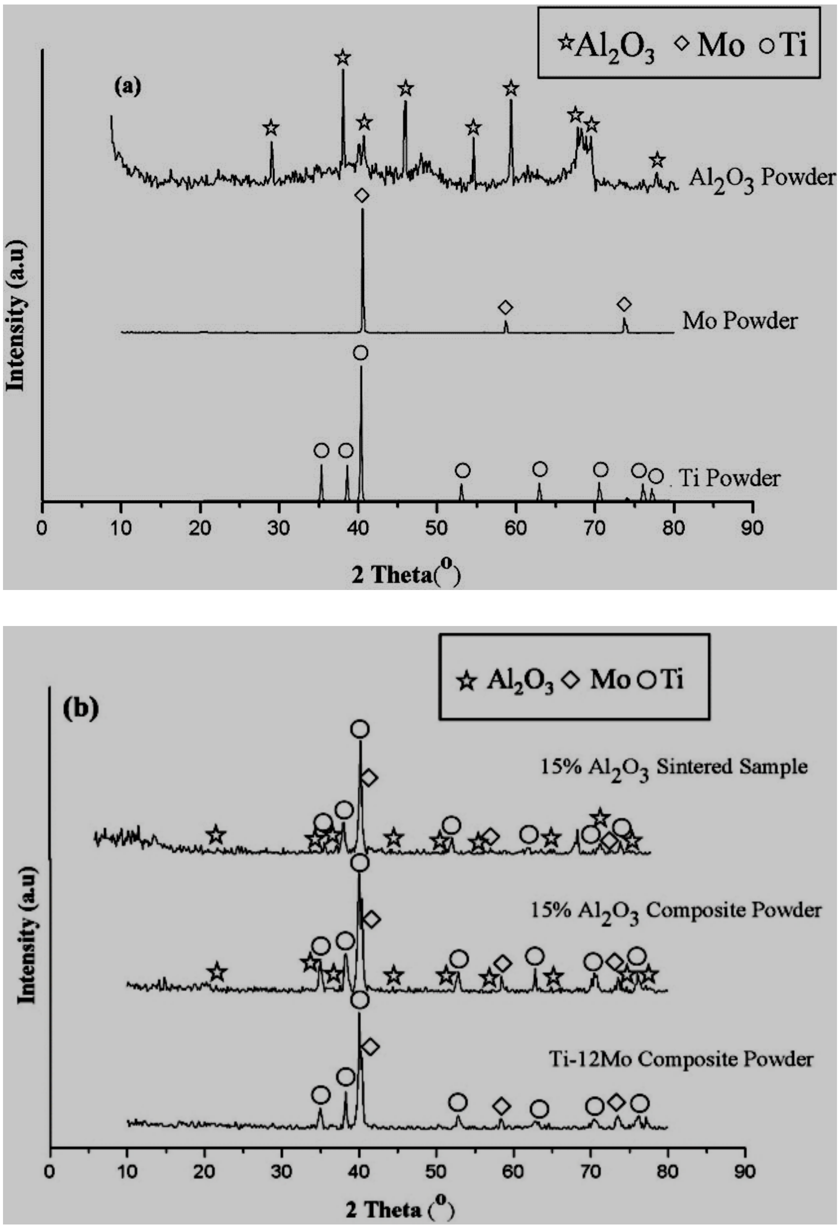

Fig. 4: XRD patterns of (a) Ti, Mo, and Al_2O_3 powders raw materials, and (b) Ti-12Mo, Ti-12Mo/15 wt. % Al_2O_3 nano-composites powder mixture, and Ti-12Mo/15 wt. % Al_2O_3 sintered nano-composite.

3.2.3. Composite Microstructure

Figure 5 shows the SEM images of the manufactured pure titanium, Ti-12Mo, and Ti-12Mo/x Al_2O_3 composites (x=5, 10 and 15 wt. %). It can be observed from image (a) that the pure Ti has (α) phase, while the microstructure of the Ti-12Mo nano-composite exhibits two phases, which are α (Ti) and γ (Mo) phases. This means that the solubility between titanium and molybdenum is limited. An excellent interface between the particles of Ti and Mo is clear from image (b), also a good distribution of Mo in the Ti matrix. A rim is formed as a result of the polishing process. By reinforcing Ti-12Mo matrix nano-composite with nano-Al_2O_3, changes on the microstructure, where the lamellar structure disappeared. Also, porosities and agglomerations of the nano-Al_2O_3 have occurred in the composites that contain alumina percentages over than 5 wt. %. The creation of pores may be due to the poor wettability between alumina, molybdenum and the titanium matrix [18].

3.3. Mechanical Properties

3.3.1. Hardness Measurement

Figure 6 shows the hardness of the Ti-12Mo and Al_2O_3 reinforced Ti-12Mo nano-composites at room temperature, compared to pure Ti. The figure shows that the hardness of the pure titanium is improved by reinforcing with 12Mo and Al_2O_3 up to 5 wt. %.

The results illustrated that the addition of 12 wt. % Mo to the pure titanium increases the hardness from 320 to 440 with a percentage of 37.5%. On the other hand, it increases from 440 to 594 with a percentage of 35% because of reinforcing it with 5 wt. % Al_2O_3. Not only the high hardness of both Mo and Al_2O_3 are the main factor that leads to enhances the hardness of pure Ti, but also the excellent interface between Mo and Ti, good distribution of Mo and Al_2O_3, and the ultra-fine particle size of them that have a great effect. In addition, the selection of suitable compaction pressure, sintering temperature, and sintering time play an important role. Regardless of the decreasing in the hardness of Ti-12Mo/Al_2O_3composite at percentages higher than 5 wt. %, yet it is still greater than that Ti-Mo composite. the agglomeration of Al_2O_3 nano-particles and the formation of the pores by increasing the Al_2O_3 content are the main factors that responsible for decreasing the hardness after 5 wt.% [19, 20], due to the non-wettability between Al_2O_3 and Ti.

3.3.2. Wear behavior

The wear rate of the Ti-12Mo/xAl_2O_3 nano-composites at 20N, 300 rpm, and 30 min is shown in figure 7 [21]. It is obvious from the results that the wear rate of pure titanium decreases by the addition of molybdenum and alumina. The incorporation of alumina into the Ti-12Mo metal matrix results in a further decrease in the wear rate. The 5 wt. % Al_2O_3 sample exhibits the lowest wear rate compared to the other 10, and 15 wt. % Al_2O_3 nano-composites. Decreasing the wear rate of the composites may be due to the high hardness of molybdenum and alumina, also may be attributed to the nano-size, good adhesion, and homogeneous distribution of Al_2O_3in the titanium-molybdenum matrix. The slight increase in wear rate of Ti-12Mo/Al_2O_3 nano-composites with Al_2O_3 content > 5% may be attributed to the powder agglomeration, which in turn increases the porosity [22].

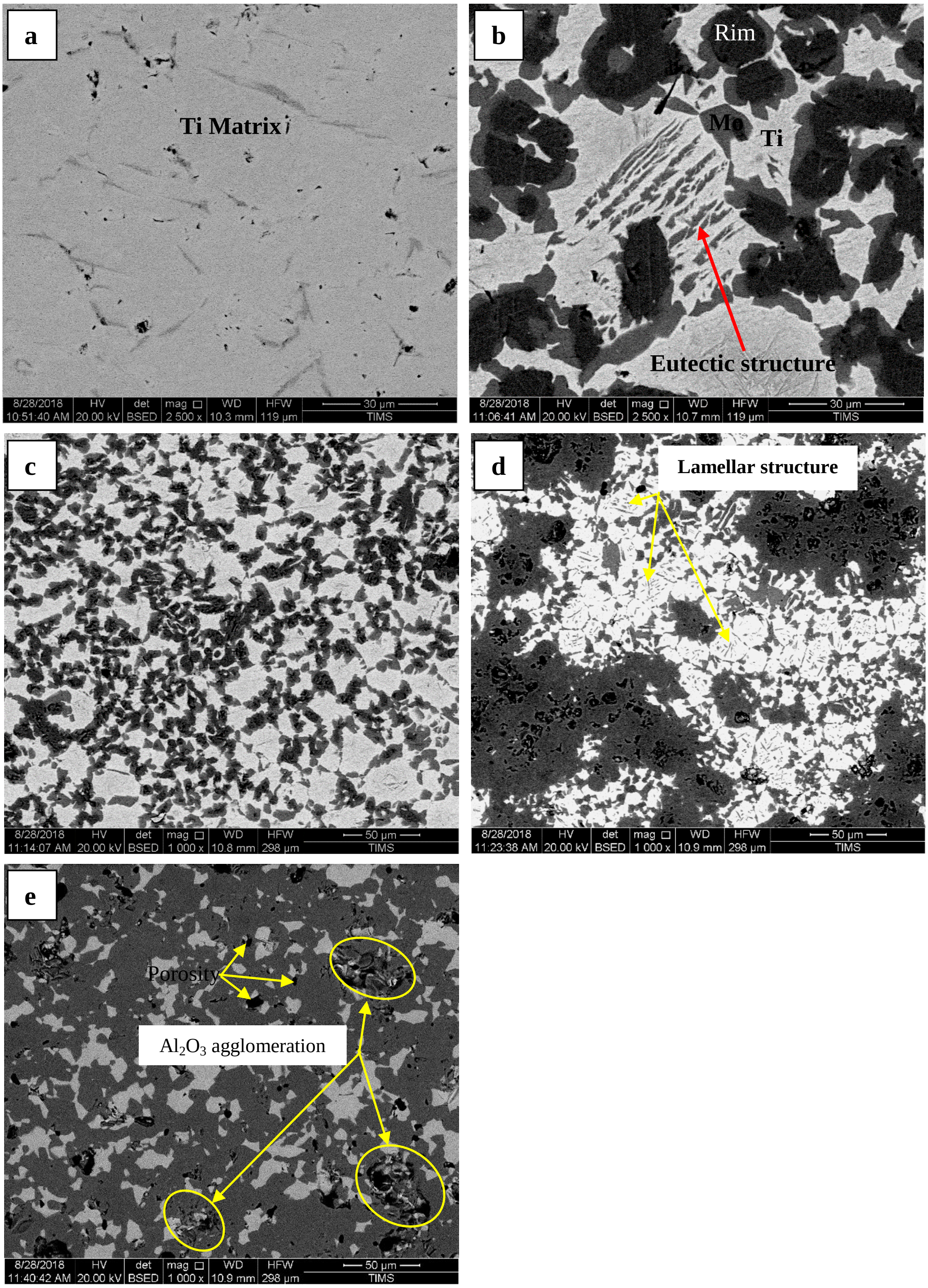

Fig. 5: SEM micrographs of (a) Ti pure, (b) Ti-12Mo, (c) Ti-12Mo/5 wt.% Al_2O_3, (d) Ti-12Mo/10 wt.% Al_2O_3 and (e) Ti-12Mo/15 wt.% Al_2O_3 nano-composites.

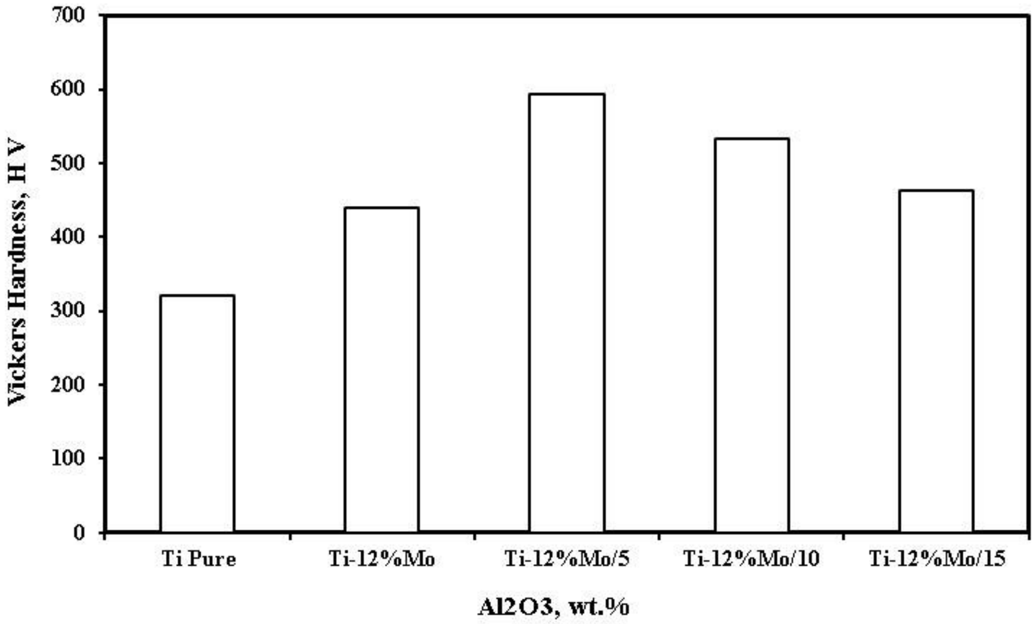

Fig. 6: Effect of Al_2O_3 nano particles content on the hardness of Ti-12Mo nano-composites.

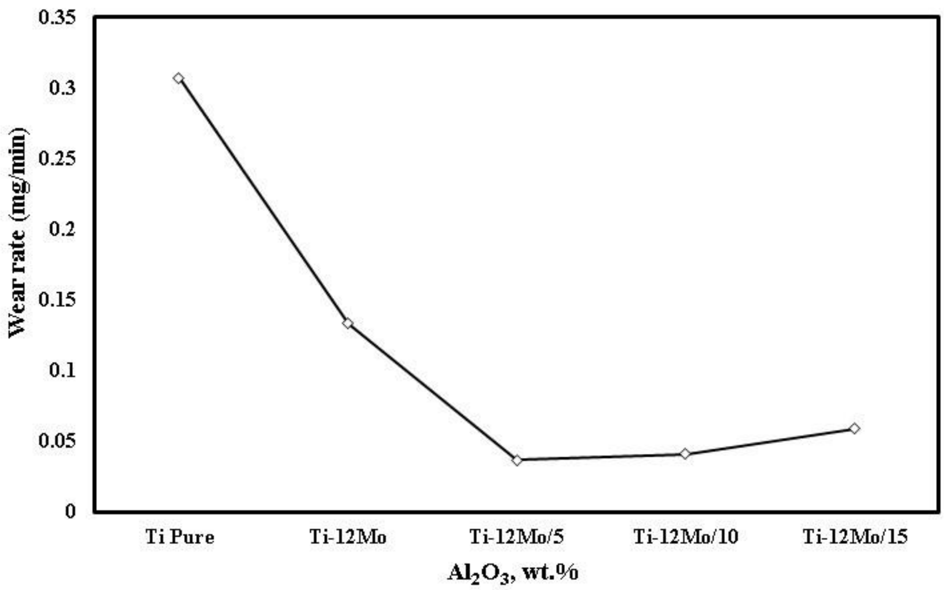

Fig. 7: Effect of Al_2O_3 content on the wear rate of the Ti-12Mo nano-composites matrix.

4. CONCLUSIONS

- To improve the mechanical properties and reduce the degradation rate of titanium matrix composite, it has reinforced with 12wt. % Mo with different weight percentages of the alumina that are 5, 10, and 15 wt. % of Al_2O_3.
- The suitable sintering temperature was at 1450°C for 90 min for fabrication Ti-12Mo/Al_2O_3 composite.
- The SEM of the 5 wt. % Al_2O_3 nano-composite shows an excellent distribution of both Mo and Al_2O_3 in the Ti matrix.
- The X-ray diffraction analysis confirmed that there are no new phases or intermetallics are formed during the sintering process.
- The relative density of pure titanium is increased by reinforcing it with 12 wt. % molybdenum and different percentages of alumina up to 5 wt. %.
- The hardness and wear resistance of the composites take the same trend, where they are increased by adding molybdenum and different percentages of the Al_2O_3 up to 5 wt.%. Regardless of decreasing the hardness and wear rate of the Ti-Mo composite after 5 wt. %, they were better than those of pure titanium were.
- Ti-12Mo/5 wt. % Al_2O_3 nano-composite exhibits the acceptable mechanical property its potential application for aerospace application.

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