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Effect of (Ge) addition on mechanical properties of (Ti12Mo5Ta) alloy used in biomedical applications

ABSTRACT

The primary objective of this investigation is to examine the impact of adding (Ge) to the Ti12Mo5Ta alloy on its compressive strength, hardness, and elastic modulus. A Ti-Mo-Ta alloy with an 83% Ti, 12% Mo, and 5% Ta composition was synthesized by powder metallurgy, with the inclusion of Ge. The mixing procedure lasted for a duration of 5 hours, with a compacting pressure of 800MPa applied to create a disk sample. After the compaction step, the samples were sintered by gradually increasing the temperature to 950 ºC at a rate of 10 ˚C/min, which took a total of 7 hours. The addition of (Ge) is done in different weight percentages, ranging from 0.5% to 5%.The impact of (Ge) was examined using X-ray diffraction. The addition of 0.5% to 5% (Ge) enhances the compressive strength of the Ti12Mo5Ta alloy. Similarly, the macro hardness of the alloy increases with higher Ge content.Conversely the inclusion of 0.5% to 5% (Ge) causes a decrease in the elastic modulus of the Ti12Mo5Ta alloy.

Keywords: *biomaterials, Compressive Strength, Macro hardness, Elastic Modules, orthopedics.*

1. INTRODUCTION

Medical specialization is continuously advancing on a daily basis. This is the rapid advancement of orthopedics, which is accompanied by the simultaneous progress in biomaterials. The term "biomaterial" was officially defined in 1982 at the "Conference of the National Institute for the Development of Consensus in Health". It refers to any substance, whether synthetic or natural, that can be used temporarily or permanently as a component of a system that treats, enhances, or substitutes any tissue, organ, or bodily function, excluding non-drugs [1]. The desire to minimize surgical interventions for the management of damaged implants has created a strong motivation for the advancement of biomaterials [2]. The national market for orthopedic implants has been steadily growing, with an estimated annual value of US $64 million. In 1999, the global value amounted to $4.4 billion.In Brazil, the annual average number of completehip prosthetic implants performed is estimated to be 24,000[3]. Metals such as (Ni), (Cr), (Ti), (W), (Fe), (Co), (Ta), (Nb), and (Mo) are used to create alloys for industrial implants that can withstand the human body [4]. Extensive study has been conducted in recent decades on Ti and Ti alloys due to its distinctive qualities. These properties encompass excellent biocompatibility, low density, high specific strength, exceptional corrosion resistance, and low Young's modulus [5,6]. Scientists have successfully created several biomaterials and technology for replacing joints in the human body, including metallic materials such as stainless steel, Co-Cr alloys, and Ti and its alloys.

The selection of these materials is primarily based on their bulk mechanical properties, which closely resemble those of human bones, as well as their inertness towards biological tissues or fluids [7]. Titanium alloys are frequently employed as substitutes for artificial bones, dental implants, and joints in the human body [6]. Commercial pure titanium (Cp-Ti), which has an α-phase type structure, was mostly utilized in orthopedic and dental applications without causing any toxicity when employed in the human body [5,8,9]. However, the mechanical properties of commercial pure titanium are insufficient for specific applications that demand both resistance to wear and high strength [10, 11]. Therefore, in order to address this issue, Ti-alloys have been engineered

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to enhance their strength [12]. In order to fulfill the specifications of biomaterials used in biomedical applications, commercial pure titanium (Cp-Ti) was substituted by the initial generation of Ti alloys, known as Ti-6Al-4V, which consist of β+α phases [13]. While several studies have examined the desirable characteristics of Cp-Ti and first-generation titanium alloy Ti-6Al-4V, there are still certain challenges that need to be addressed. Recent research indicates that the Cp-Ti (α-phase) and Ti-6Al-4V (α+β phase) alloys have an elastic modulus of 100 GPa, which surpasses the bone's modulus of elasticity of 20 GPa. This discrepancy results in a stress shielding effect. This stress results in bone and implant loss [5, 14,15]. In order to address these problems, numerous studies have concentrated on developing various titanium-based alloys that possess a low Young's modulus, non-allergenic and non-toxic components, and a single phase [16,17]. As a result, scientists have conducted thorough research on a type of titanium biomaterials called β-titanium alloys. These alloys possess a low elastic modulus and consist of non-toxic metals such as (Mo), (Zr), (Nb), and (Ta). They are now undergoing research to determine their possible applications in the field of biomedicine. [16, 18, 19]. According to the paper, Ti alloys of the second generation β or close β have been found to have notable benefits for biomedical purposes [20]. Nevertheless, there exist many compositions of β titanium alloys, each with distinct microstructures including β, β+α, β+α', β+α'', and β+ω [21].

2.EXPERIMENTAL WORK

The Ti 12Mo5Ta –xGe alloys were utilized to create the specimens by the powder metallurgy process. The mean particle size and level of purity of the samples are provided in Table (1). The weighted powders were meticulously mixed using a rotating automatic ball mill, employing steel balls of different sizes. Ethanol was introduced as a wet mixing medium. The procedure of mixing was conducted for a duration of 5 hours. After the mixing process, 3.5 grams of powder were taken and compressed with an electric hydraulic press to form a sample of 12 mm in diameter and 6 mm in thickness. The pressure applied during compaction was 800 (MPa), and the sample was held under this pressure for a duration of 4 minutes. The sintering process was conducted in an electrical argon furnace under Argon conditions. After the compaction stage, the samples were sintered by increasing their temperature to 950 ºC at a heat rate of 10 ˚C/min. The samples were thereafter immersed for a duration of 7 hours and then cooled within the furnace until they achieved ambient temperature.

Table 1. Materials powder used in this work, together with their average particle size and purity.

Powder	Ti	Mo	Ta	Ge
Average particle size (μm)	26.43	29.89	6.433	4.325
Purity %	99.85	99.90	99.95	99.97

2.1.Microstructures characterization

X-Ray Diffraction

The Ti alloy underwent X-ray diffraction examination after sintering, and the obtained data were compared with standard charts. The test was conducted with a speed of 6 degrees per minute, a step size of 0.02 degrees, and an angle range of 20-80 degrees with a copper (Cu) target. The wavelength employed was 1.54060 Angstroms, the voltage was 40 kilovolts, and the current was 30 mill amperes.

Microstructure Observation

After the sintering process, all samples were subjected to grinding using silicon carbide sheets with varying grit sizes, namely 180, 400, 600, 800, 1000, 1200, 1500, and 2000. Afterwards, the samples were polished using diamond paste in order to attain a glossy and reflective finish, which served as the final phase. The etching process was conducted at ambient temperature. The chemical composition of the etching solution is presented in table 2 [22]. Following the etching process, the specimens were rinsed with water, dried, and examined using a Light Optical Microscope. Characteristics such as the identification of phases, shape, and grain size are included in the analysis of grain boundaries. Each of these possesses unique attributes. The microstructure was examined at a magnification of 400x using an Olympus microscope.

Table 2. Etching solution composition [22].

NO	Constituents	ml
1	HF	10 ml
2	HNO_3	5 ml
3	H_2O	85 ml

2.2.Compressive strength

The Compression test was conducted at the temperature of the surrounding environment, as specified by ASTM B925–08. Specimens with a diameter of 12 mm and a height of 18 mm were produced for this experiment. The experiment was carried out with a computer-controlled electronic universal testing machine model (WDW-200KN). A universal testing machine was employed to measure the rate of load speed, which was set at 0.5mm/min. The compressive strength of the samples can be determined using the following formulae [23]:

Compresive strength =
= (Max.force)/(crosssectional area) (1)

2.3.Macro- hardness measurement

Prior to the test, the specimens underwent proper grinding and polishing. The experiment was conducted on the prepared samples. The Brinellmacro hardness test involves applying a load of 62.5 kg/mm² to the specimen and measuring its hardness using a carbide ball with a diameter of 2.5 mm for a duration of 10 seconds. An average of three readings was taken to determine the hardness of each specimen.

2.4.Elastic modules

The ultrasonic wave test is employed to measure the modulus of elasticity. This test involves the use of ultrasound waves that traverse the specimen from one side to the other, representing the length of the specimen (L). The passage time of the wave through the sample is measured using electronic time instruments. The specimen utilized in this test has a diameter of 12mm and a length of 18mm. Various equations are employed to calculate the modulus of elasticity, as outlined in reference [24].

$$E = \frac{\rho V_S^2 \left(3V_L^2 - 4V_S^2\right)}{V_L^2 - V_S^2} \quad (2)$$

The symbol E denotes Young's modulus of the alloy, whereas the symbol ρ represents the density of the alloy. V_L refers to the velocity of longitudinal ultrasonic waves, while V_S denotes the velocity of shear ultrasonic waves. Equations 3 and 4 were utilized to determine the values of V_L and [24].

$$V_L = 2\, l / t_L \quad (3)$$

$$V_S = 2\, l / t_S \quad (4)$$

The variable t_L denotes the transit time of longitudinal ultrasonic waves, t_S denotes the transit time of shear ultrasonic waves, and l represents the thickness of the samples.

3. RESULT AND DISCUSSION

3.1.Microstructure characterization

The (XRD) patterns of the green compact alloys exhibit only the presence of titanium (Ti), molybdenum (Mo), tantalum (Ta), and germanium (Ge) phases. This is because there is no occurrence of phase change during the compacting process. Phase transformation is a type of diffusion process that requires a high temperature in order to take place. Figure (1) displays the (XRD) patterns of the base alloy (Ti12Mo5Ta) after undergoing sintering at a temperature of 950 °C for a duration of 7 hours in an argon atmosphere. It is evident that Ti, Mo, and Ta underwent transformation into two solid solutions, namely αTi and βTi.

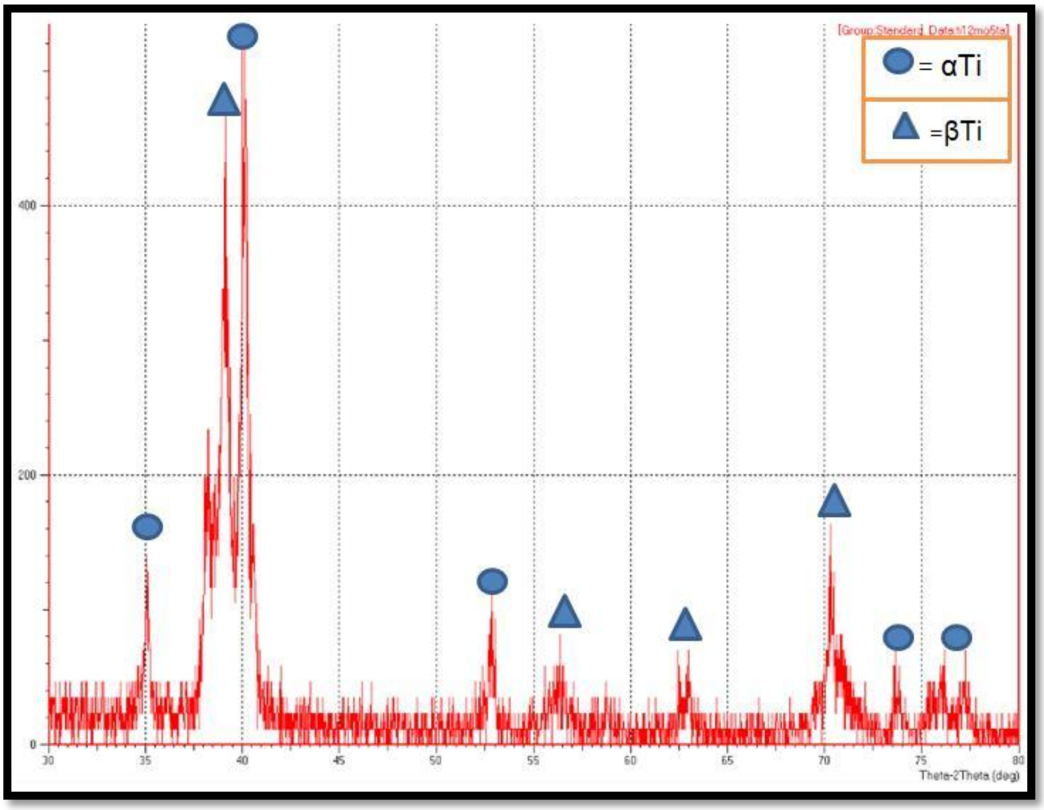

Figure 1. XRD patterns of (Ti12Mo5Ta) After Sintering Process

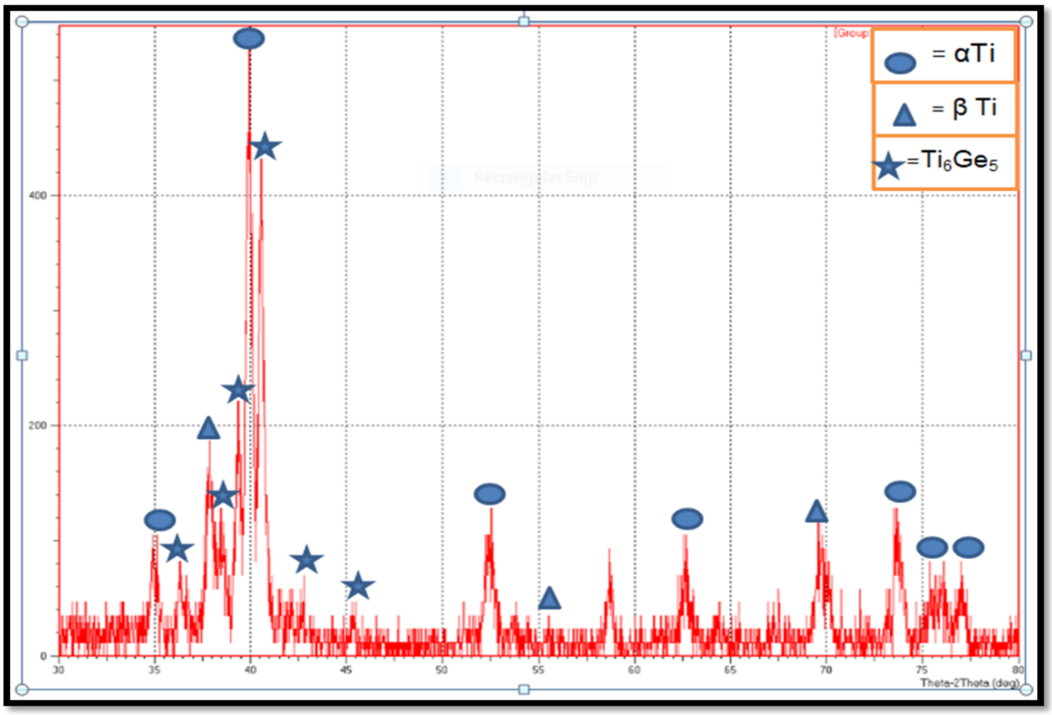

Figure 2. XRD patterns of (Ti12Mo5Ta) with 5% Ge after the sintering process

Figure (2) depicts (XRD) pattern of the base alloy (Ti12Mo5Ta) with 5% Ge after undergoing the sintering process at a temperature of 950°C for a duration of 7 hours in an Argon gas atmosphere. The graphic displays the transformation of the basic elemental substances Ti, Mo, Ta, and Ge into αTi, βTi, and Ti_6Ge_5. However, the figure does not show any peaks corresponding to metallic Ti, Mo, Ta, and Ge. The sintering process length of 7 hours was sufficient to fully complete the phase transformation process, as it enhanced the interdiffusion between (Ti), (Mo), (Ta), and (Ge). The presence of free elements in alloys used as biomaterials is avoided due to their harmful effects on the organism.

Figures (3 - 8) display the microstructure of etched alloys following the sintering process, both with and without the addition of Ge, at a magnification of 400X. The borders of the grains and the existing phases were identified by examining the microstructure of these alloys. The specimens, after undergoing the sintering process, were found to possess a microstructure consisting of two distinct regions, known as a duplex microstructure. One part appears light (bright) and consists of the α-Ti phase, while the other sections appear dark, indicating the presence of the (β-phase).

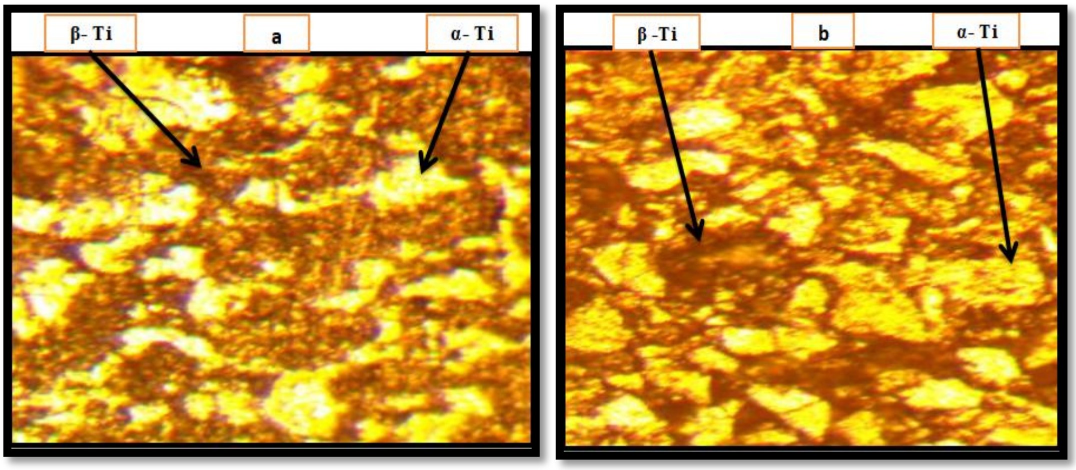

Figure 3. Microstructure of etched base alloy (a) and 0.5%Ge (b) after sintering process at 400X magnification

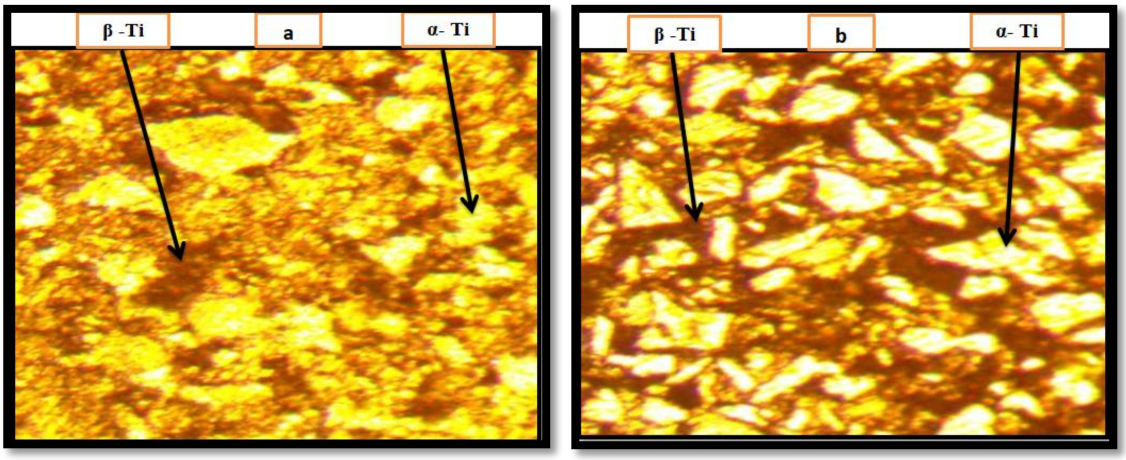

Figure 4. Microstructure of etched 1%Ge (a) and 1.5%Ge (b) after sintering process at 400X magnification

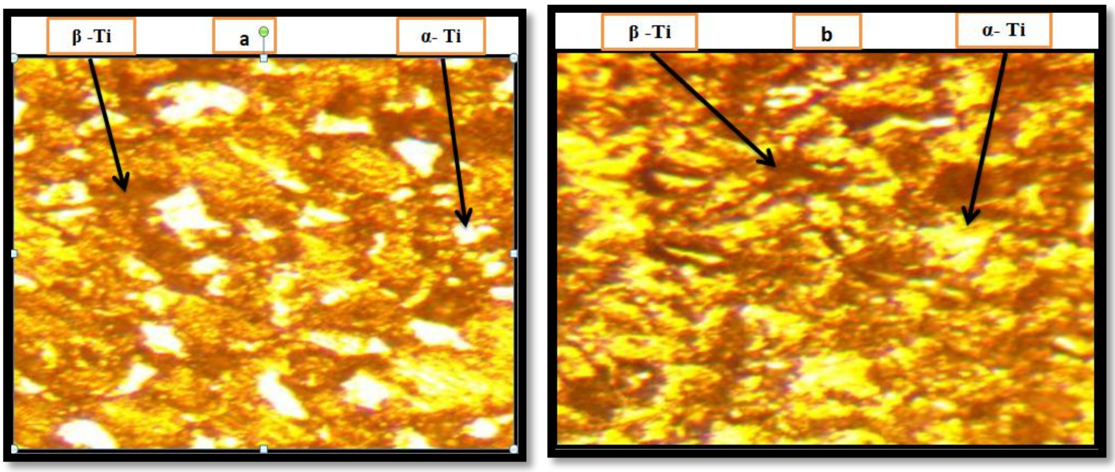

Figure 5. Microstructure of etched 2%Ge (a) and 2.5%Ge (b) after sintering process at 400X magnification

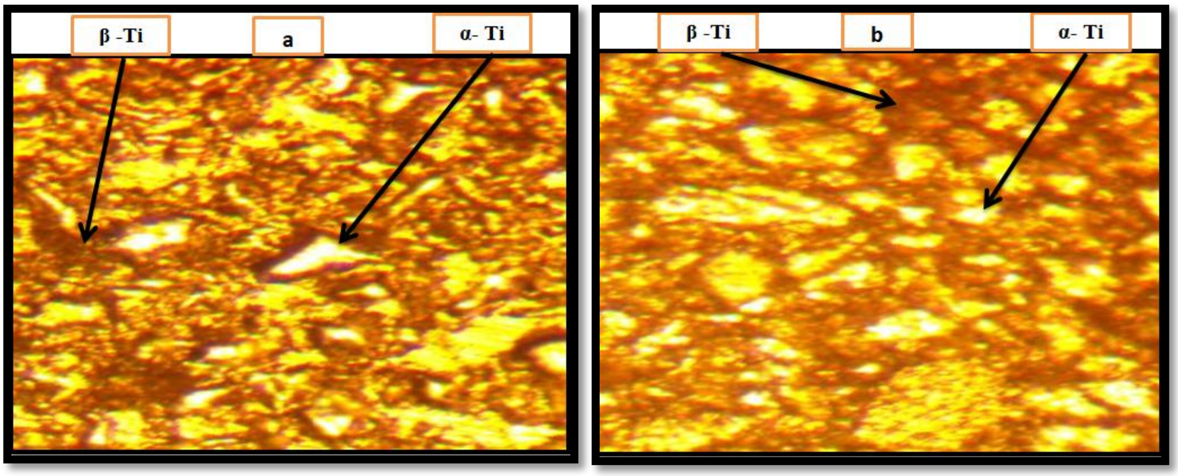

Figure 6. Microstructure of etched 3%Ge (a) and 3.5%Ge (b) after sintering process at 400X magnification

The presence of Mo and Ta elements results in the promotion of the dark reign (β-phase) due to their role as stabilizing factors for the β phase. By increasing the quantity of germanium, the shaded region is raised. At room temperature, there are some beta phases in equilibrium, which is analogous to α- β and β alloys [25]. The use of the powder metallurgy process in alloys results in a uniform distribution of the strengthening phase throughout the matrix, Consequently, enhancing the alloys' ability to withstand wear and boosting their mechanical characteristics. The microstructure demonstrates the presence of intermetallic phase (Ti_6Ge_5) as depicted in XRD figure (2), resulting in enhanced hardness of the alloy and improved mechanical properties with higher germanium content.

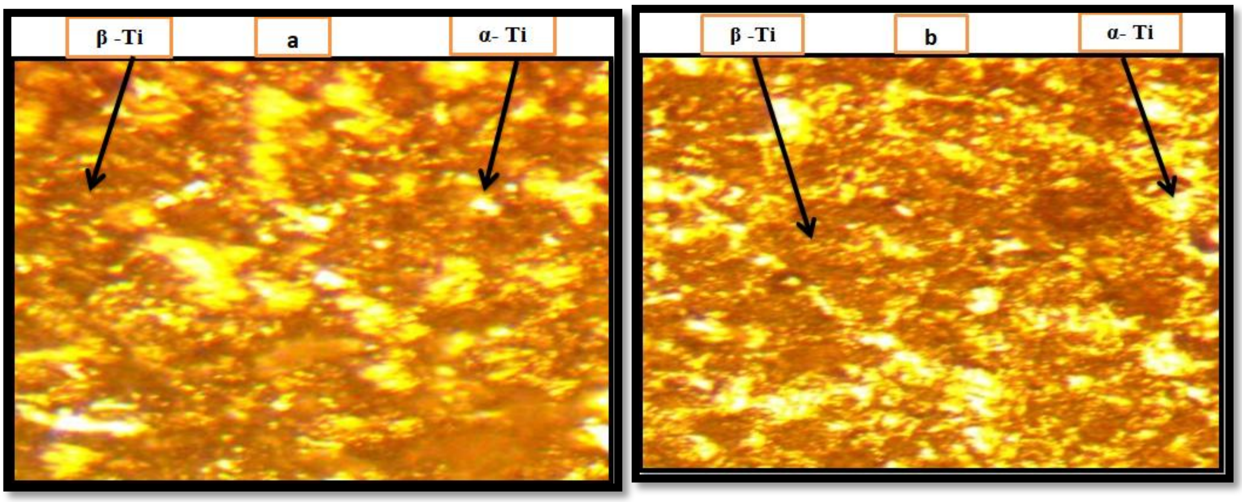

Figure 7. Microstructure of etched 4%Ge (a) and 4.5%Ge (b) after sintering process at 400X magnification

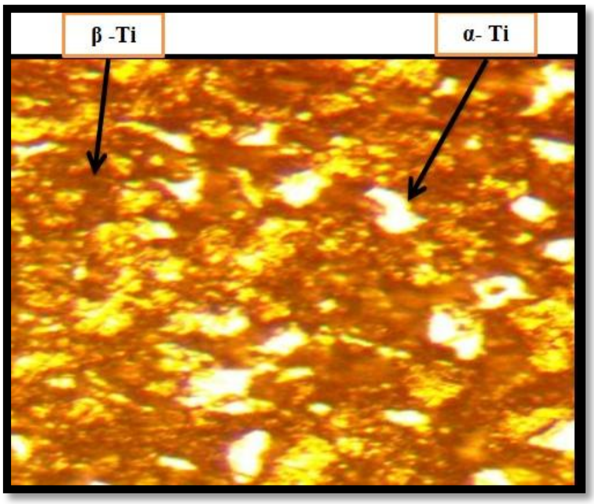

Figure 8.Microstructure of etched 5% after sintering process at 400X magnification

Table 3. Compressive strength, porosity, and improvement Vs Germanium contents

Ge(%)	Porosity (%)	Compressive Strength (MPa)	Improvement in Compressive Strength (%)
0	33.4	280	
0.5%	32.7	290	3.57
1%	30.4	305	8.92
1.5%	28.2	325	16.07
2%	26.4	355	26.78
2.5%	25.6	360	28.57
3%	23.9	395	41.07
3.5%	22.2	410	46.42
4%	21.6	428	52.85
4.5%	20.1	435	55.35
5%	18.7	466	66.42

3.2.The compressive strength

The compressive strength of the base alloy (Ti12Mo5Ta) increased from 280MPa to 466MPa, a 66.42% improvement, as the Germanium content increased up to 5%. This improvement can be attributed to the addition of Germanium, which resulted in the Creation of intermetallic compounds (specifically Ti_6Ge_5) that strengthened the alloy. Additionally, increasing the Germanium content led to a decrease in the percentage of porosity.Porosity and resistance to compression have an inverse relationship. Table (3) displays the compressive strength, percentage of porosity, and percentage of improvement for the alloys utilized.

3.3.Macro-hardness measurement

The Brinell hardness test was used to measure the hardness of specimens made of the basic alloy (Ti12Mo5Ta) and specimens with the addition of Ge. The addition of Germanium to (Ti12Mo5Ta) resulted in an Augment in hardness. As the Germanium content increased, the hardness also increased. This can be attributed to the strengthening effect of the intermetallic compound (Ti_6Ge_5). The maximum improvement in hardness was observed with a 5% Germanium addition, resulting in a hardness of 290 Kg/mm^2, which corresponds to a 56.75% increase. This information is presented in table (4).

Table 4. Improvement percentage in hardness according to Ge contents

Ge (%)	HB	Improvement (%)
0	185	
0.5%	194	4.86
1 %	212	14.59
1.5%	220	18.91
2%	234	26.48
2.5%	246	32.97
3%	256	38.37
3.5%	268	44.86
4%	274	48.1
4.5%	281	51.89
5%	290	56.75

3.4. Elastic modules

The elastic characteristics can be ascertained, and the findings are presented in table (5).

Table5. Presents the elastic modulus of the produced alloys

Ge(%)	Elastic Modulus (GPa)	Improvement in Elastic Modulus (%)
0	95.67	
0.5%	89.44	6.51
1%	83.56	12.65
1.5%	77.41	19.08
2%	72.32	24.40
2.5%	68.43	28.47
3%	62.82	34.33
3.5%	57.91	39.46
4%	51.87	45.78
4.5%	48.64	49.15
5%	42.67	55.39

The correlation between the elastic modulus and the concentration of Germanium is such that as the Germanium content increases, the elastic modulus drops. This decrease can be described as follows: The atomic radii of Ti, Mo, Ta, and Ge are 0.147 nm, 0.139 nm, 0.149 nm, and 0.137 nm, respectively. By adhering to Vegard's law, the arrangement of Ge atoms causes the host lattice to expand, resulting in a linear growth of the lattice parameter of the bcc phase. This rise in parameter weakens the bonding force between the adjusted atoms [26]. Conversely, the rise in Germanium concentration resulting from the increase in the dark reign (β-phase) must lead to “a drop” in the elastic modulus. Nevertheless, the porosity of the (Ti12Mo5Ta) alloys decreases as the Germanium concentration increases, resulting in a drop in the elastic modulus, as indicated in table (5). The key factors contributing to the drops in the elastic modulus in elastic modulus of the porous (Ti12Mo5Ta) alloys with increasing Germanium levels are the combination of phase compositions (namely the β-phase) and the presence of porosity, which reached a level of 33.4%. The drops in the elastic modulus of (Ti12Mo5Ta) alloys enhances their suitability for surgical implant applications by mitigating the stress-shielding effect, which has detrimental effects on bone tissues [27].

4. CONCLUSION

1-The inclusion of germanium improved the compressive strength of the (Ti12Mo5Ta) alloys. The strength increased as the germanium concentration increased, reaching a maximum value of 466MPa at 5% germanium. This represents a 66.42% boost in strength.

2- The inclusion of Germanium enhanced the macro hardness of the (Ti12Mo5Ta) alloy, with hardness increasing proportionally to the Ge content. The alloys reached a maximum hardness value of 290Kg/mm^2 with a Ge content of 5%, resulting in a significant improvement of 56.75%.

3- The inclusion of Germanium was improved. The Elastic Modulus of the (Ti12Mo5Ta) alloy reduces as the Ge content increases. The minimum Elastic Modulus value was 42.67GPa at 5% Ge, with an improvement percentage of 55.39%.

4- The inclusion of Germanium to (Ti12Mo5Ta) alloy results in the formation of the (Ti_6Ge_5) phase, which leads to a change in properties.

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IZVOD

UTICAJ DODAVANJA (Ge) NA MEHANIČKA SVOJSTVA LEGURE (Ti12Mo5Ta) KOJA SE KORISTI U BIOMEDICINSKIM APLIKACIJAMA

Primarni cilj ovog istraživanja je da se ispita uticaj dodavanja (Ge) leguri Ti12Mo5Ta na njenu čvrstoću na pritisak, tvrdoću i modul elastičnosti. Ti-Mo-Ta legura sa sastavom 83% Ti, 12% Mo i 5% Ta je sintetizovana metalurgijom praha, uz uključivanje Ge. Procedura mešanja je trajala 5 sati, uz pritisak sabijanja od 800 MPa da bi se napravio uzorak diska . Nakon koraka sabijanja , uzorci su sinterovani postepenim povećanjem temperature na 950 ºC brzinom od 10 ˚C/min, što je ukupno trajalo 7 sati. Dodatak (Ge) se vrši u različitim težinskim procentima, u rasponu od 0,5% do 5%. Uticaj (Ge) je ispitan korišćenjem rendgenske difrakcije . Dodatak od 0,5% do 5% (Ge) povećava čvrstoću na pritisak legure Ti 12Mo5Ta. Slično tome , makro tvrdoća legure raste sa većim sadržajem Ge . Suprotno tome, uključivanje od 0,5% do 5% (Ge) uzrokuje smanjenje modula elastičnosti legure Ti12Mo5Ta.

Ključne reči: *biomaterijali, čvrstoća na pritisak, makro tvrdoća, elastični moduli, ortopedija*

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