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Article · July 2018

DOI: 10.12693/APhysPolA.134.415

5 authors, including:

Angélica Amigó
Universitat Politècnica de València

Angel Vicente-Escuder
Universitat Politècnica de València

Vol. **134** (2018) *ACTA PHYSICA POLONICA A* No. 1

Special Issue of the 7th International Advances in Applied Physics and Materials Science (APMAS 2017)

Investigations of Ti Binary Alloys Manufactured by Powder Metallurgy for Biomaterial Applications

H.Y. Atay[a,*], M.H. Rodríguez[b], A.A. Mata[b], A.V. Escuder[b] and V.A. Borrás[b]
[a]İzmir Katip Çelebi University, Department of Material Science and Engineering, 35620 Çiğli, İzmir, Turkey
[b]Universidad Politécnica de Valencia, Departamento de Ingeniería Mecánica y de Materiales, 46022 Valencia, Spain

Biomaterials encompass synthetic alternatives to the native materials found in our body. They have shown rapid growth in the field of elderly population demands with the prolongation of human life. Titanium is one of the biomaterials with excellent properties and biocompatibility. However, its high stiffness may cause weakening in the structures. To sort out this problem, Ti-Cr, Ti-Mo, and Ti-Cu alloys were produced by powder metallurgy. Metal powders were mixed by mechanical alloying. After pressing and sintering, characterizations were carried out by scanning electron microscopy, X-ray diffraction, electron backscattering diffraction, and three points bending test.

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PACS/topics: titanium alloys, Ti-Cu, Ti-Cr, Ti-Mo, powder metallurgy, biomaterials

1. Introduction

Biomaterials help in improving the quality of life of the elders. As the world population is getting older, the demand for those materials is rapidly increasing [1, 2]. Titanium alloys have become very attractive as one of the biomaterials due to their lightweight, high bio-corrosion resistance, biocompatibility and mechanical properties. Actually, pure titanium has also established a reputation for excellent biocompatibility as a dental metal, being suitable for prosthetic dental applications. However, some inherent problems must be overcome for titanium to be used successfully such as its stiffness, high melting temperature and high reactivity with oxygen and impurities at elevated temperatures [3, 4]. Producing titanium alloys can be one of the solution to alter its properties, namely to improve strength, high-temperature performance, creep resistance, weldability and formability [4]. Producing titanium alloys can be useful for reducing stiffness valuations.

In this study, Cr, Mo and Cu were chosen for producing binary Ti alloys as alternatives capable of satisfactorily replacing the traditionally used alloys. Those elements are known for increase of stabilizing β phase of titanium. These phases of titanium alloys are more appropriate for bio-applications. The presence of titanium body centered cubic crystal structure (β phase) at room temperature leads to decrease of elastic modulus and improves the stress shielding problem, therefore β type titanium alloys could be produced with lower modulus of elasticity and greater strength [5]. Copper also offers the possibility to be bactericidal. Ti-Cr alloys were reported to have high tensile strength and good ductility for dental casting alloys. It was observed that the hardness of the Ti-Cr alloys became greater as the Cr content increased [6]. The addition of Mo decreases the elastic modulus of the alloys. Also, Mo is a refractory element with a high melting point, and the addition of Mo can also enhance the strength and abrasion resistance of Ti-based alloys [7]. The fusion temperature of Ti-Cu alloy decreases with an increase in the amount of copper [8]. Titanium alloyed with a small amount of copper is reported to have adequate biocompatibility and corrosion resistance for dental use [9]. Regarding the production method, powder metallurgy was used. After pressing and sintering different combinations of titanium alloys were produced with Cr, Mo, and Cu elements. Characterizations of the specimens were carried out, scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDX), electron backscattering diffraction (EBSD), optical microscope and three points bending test.

2. Materials and methods

The experimental program was composed of mixing, mechanical alloying of powders, and press and sinter process. Elemental powder mixtures were prepared as the following: Ti5Cr, Ti9Cr, Ti13Cr, Ti6Mo, Ti12Mo, Ti21Mo, Ti5Cu, Ti7Cu and Ti12Cu in weight. Three alloys were prepared for each composition ratio. Mechanical alloying was performed in a planetary ball mill model PM 400/2 Retsch using a rotation speed of 300 rpm by using pure titanium, chromium, molybdenum and copper powders. The ball to powder weight ratio was 10:1. The milling batch had a mass of 20 g for each run. To prevent an excessive temperature rise of the powder during milling, milling was stopped at 45 min, and then the grinding bowl was allowed to cool for 20 min. To minimize powder oxidation, milling was carried out under an argon atmosphere. The die for mechanical pressing has a rectangular shape with dimensions of 30 $\times 12$ mm^2. It was filled with approximately 7 g of powder with the height of 5 mm. Compaction was

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[*] corresponding author; e-mail: `hgulyilmaz@gmail.com`

applied in hydraulic press, Instron model 1343, which has a range of use of ±500 kN for static trials. A pressure of 600 MPa is used for compaction of test specimens. Sintering was performed in a high vacuum Carbolite model HVT15/75/450 tubular furnace. Sintering cycle of process for Ti-Cr and Ti-Mo alloys was as the following: a rise 15 °C/min, to reach them 750 °C that is keep ones 30 min to get a homogenization of the temperature, continue with a rise to 10 °C/min, until them 1250 °C that is maintain 180 min and then the cooling in oven. For Ti-Cu alloy the sintering temperature was 950 °C. The porosity is estimated by the Archimedes method for open and closed porosities. Pore diameter and circularity were measure by optical microscopy. The bending test is performed with rectangular samples $30 \times 12 \times 5$ cm^3, at a speed of 1 mm/min, obtaining the stress, strain and flexural modulus of each of the alloys studied. The elastic modulus was obtained by ultrasounds methodology.

3. Results and discussions

Figure 1 depicts the distribution of the alloying elements before sintering. Mechanical alloying provides homogeneous distribution. It can be seen from the figure that addition of Cu is greater intimacy with Ti. It is mainly due to the higher ductility of this element. The particles are randomly distributed within TiCr and similar particle size with Ti. In TiMo system, elements are preferably distributed on the surface of the particles of Ti. Therefore we can say that the TiMo is a better mix but compaction is not as good as the TiCr and TiCu.

Table 1 demonstrates the pores and densities of the alloys. As can be seen, TiCu alloy has lower porosity than other alloys due to its greater plasticity. Furthermore, the porosity decreases with increase of percentage of the alloys. The pore size obtained is smaller diameter and very close to the spherical shape. By contrast in the alloys of Cr and Mo, the porosity is greater and the pores have a larger diameter and more elongated shapes in TiCu alloys. This is due to the greater hardness of alloying and its worst compaction of the mixture. Relative density values are very close for three alloys. For TiCu and TiMo alloys, the density increases with increase of the amount of element. However, the densities obtained in the TiCr alloys practically remain the same about 92%.

Figure 2 demonstrates the microstructures of the alloys. In TiCr and TiMo systems microstructures are formed by $\alpha + \beta$ phases, α phase (dark) and β phase (light). TiCr has 75% α phase, for content of 5% Cr. It decreases to 20% when the Cr content is 13%. Similarly for Mo alloys, α phase decreases when Mo content increases. Stabilization of β phase is observed by the addition of Mo. Addition of Cr with microstructures β grains provides formation of α phase in grain boundaries. The decrease of the alpha phase takes place by a stabilization of the beta phase by increasing the content in the alloying element or by the formation of the corresponding intermetallic phase [10, 11].

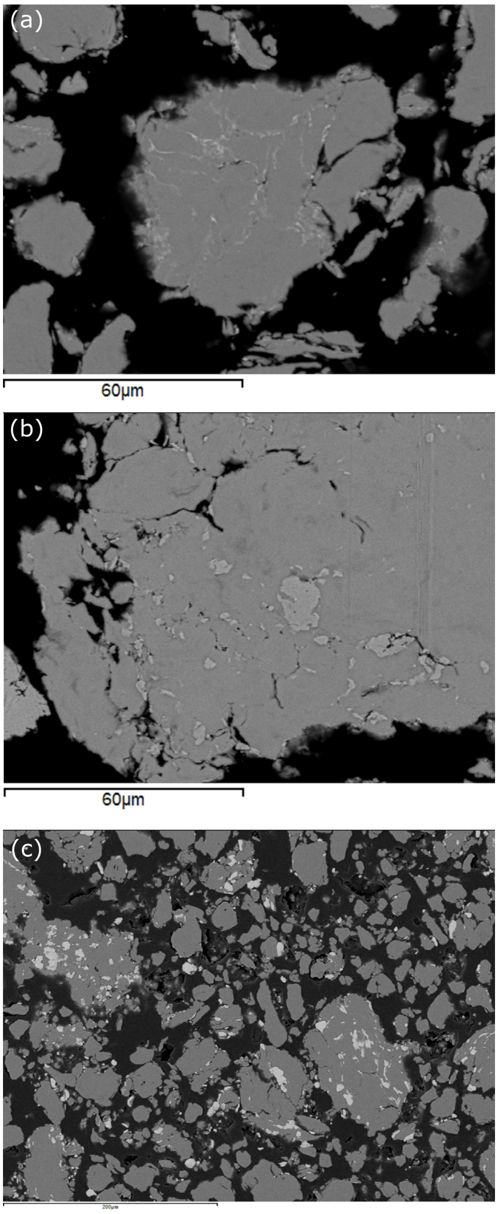

Fig. 1. Backscattered image of those powder mixtures: (a) Ti5Cu, (b) Ti5Cr, (c) Ti12Mo.

TABLE I

Estimations of pores and densities of the alloys

Alloys	Exp. density [g/cm^3]	Relative density [%]	Pore ø [μm]	Pore circularity
Ti6Mo	4.11	88.12 ±0.69	3.66	0.86
Ti12Mo	4.50	93.21 ±0.88	2.22	0.95
Ti21Mo	4.81	94.06 ±0.43	1.94	0.97
Ti5Cr	4.25	92.62 ±0.88	4.32	0.85
Ti9Cr	4.29	92.00 ±0.73	2.65	0.92
Ti13Cr	4.39	92.65 ±0.72	3.37	0.88
Ti5Cu	4.43	95.90 ±0.23	2.25	0.93
Ti7Cu	4.58	98.04 ±0.23	1.64	0.99
Ti12Cu	4.78	99.73 ±0.09	1.58	0.99

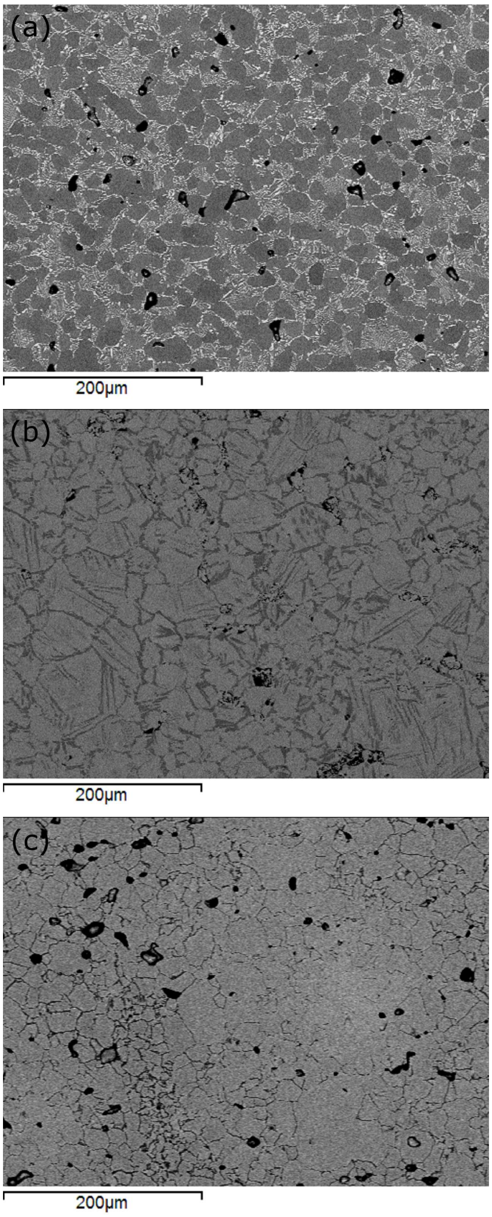

Fig. 2. SEM images of the phase distribution in different alloys: (a) Ti12Cu, (b) Ti13Cr, (c) Ti21Mo.

The formation of the mentioned $\alpha+\beta$ phases in the TiCr and TiMo alloys is confirmed by X-ray diffraction, Fig. 3, as reported Hsu et al. [6] and Lu et al. [7]. The microstructure corresponds to 90% phase for 5% by weight of Cu. By increasing the content of Cu, the amount of α phase decreases to 78%, with formation of eutectoid $Ti_2Cu+\alpha$. Ti_2Cu intermetallic formation decreases the porosity of the TiCu alloys. The microstructure in the TiCu alloys correspond to α grains intermetallic Ti_2Cu by cleaving the beta phase at elevated temperature.

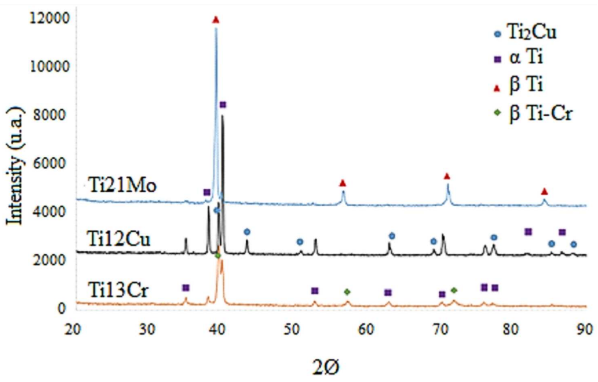

Fig. 3. Diffraction patterns of the alloys.

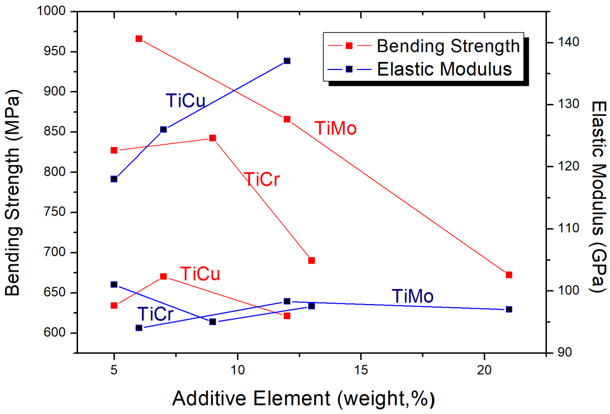

Fig. 4. Bending strength and elastic modulus vs. content of elements.

The results of bending tests and elastic modulus are seen in Fig. 4. The Ti-Cu alloys have the lowest bending strength, around 650 MPa. However, maximum bending strength of the TiCr and TiMo alloys decreased with increasing alloying element content. In the latter two systems for the lower contents of Cr or Mo have bending strength of 830 and 960 MPa, respectively, decreasing to values of 670–680 MPa for higher content tested. This significant reduction in the maximum bending strength of the TiCr and TiMo alloys can be explained by the stabilization of the β phase [6, 7]. Not only the phase effect the bending strength, additives also change the grain size. Ductility obtained in the three systems is insufficient for applications where elongation is necessary. The maximum value obtained is 4.2% for TiCr alloys and 2–3% for the other alloys. A dual behavior is obtained for elastic modulus analyzed by ultrasound techniques. While TiCr and TiMo systems is slightly lower than the commercially pure Ti, remains around 95–98 GPa. The TiCu system substantially increases the elastic modulus from 118 GPa to higher values 135 GPa for 13 wt% of Cu.

EBSD analysis results of the alloys are demonstrated in Fig. 5. XRD and SEM analysis results mentioned above are supported with this analysis. In TiCr alloy, Ti-hexagonal structure has 001, TiCr2 intermetalic phases 010 and TiCr alloys has 120 and 111. Abundant phases are Ti-hexagonal and TiCr alloys. There is no any Ti-

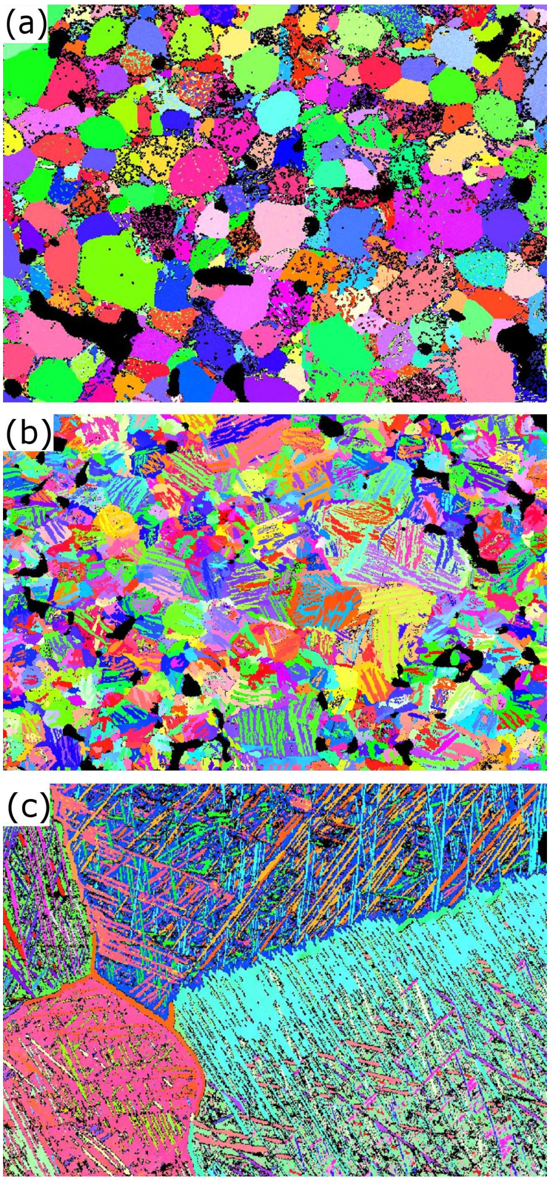

Fig. 5. Inverse pole figures of the alloys: (a) Ti12Cu, (b) Ti9Cr, (c) Ti21Mo.

cubic phase. $TiCr_2$ hexagonal and $TiCr_2$ intermetallic phases have trace amount. Ti-hexagonal phase has 51% and TiCr has 41% phase fraction. In TiMo alloy, abundant phases are titanium cubic and Ti-hexagonal. Ti-hexagonal phase has 39%, titanium cubic 30%, and Ti-α 10% phase fractions. In Ti-Cu alloy, abundant phase is Ti-hexagonal with the value of 90%. Ti_2Cu is 10% and the rest is titanium cubic phase.

If all these results are to be evaluated, it will not be easy to indicate any alloy as the best biomaterial candidate. It must be decided according to use conditions of the alloy, such as where and how the alloy will be used. Although the environment seems to be the same body for a biomaterial, the enzymes, pressure, temperature, etc. in the hip region may be different in the mouth or on the knee. In addition, whether the material to be used is movable or stationary will also change the required properties of the material.

4. Conclusions

Ti-Cr, Ti-Mo and Ti-Cu alloys were produced by powder metallurgy. Metal powders were mixed by mechanical alloying before pressing and sintering. TiCu powder after mechanical alloying presents more intimate union with Ti particles than the other powders. TiCr and TiMo systems obtain two phases: α phase (dark) and β phase (light). A mixture of α phase and Ti_2Cu intermetallic is observed on the microstructure of TiCu alloys. In all cases β phase or Ti2Cu increase with higher content of alloying element. The bending strength decreases generally, with the increase of elements addition. Elastic modulus decreases with Cr and Mo addition due to β phase stabilization. However, Cu addition increases the elastic modulus regarding commercially pure Ti due to the formation of intermetallic Ti2Cu.

Acknowledgments

The authors thank the Ministerio de Economia y Competitividad of Spain for the research project MAT2014-53764-C3-1-R, An European Commission by FEDER funds for the purchase of equipment, the Generalitat Valenciana by the PROMETEO/2016/040 project.

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