

Mater. Res. Soc. Symp. Proc. Vol. 1766 © 2015 Materials Research Society
DOI: 10.1557/opl.2015.406

Study Microstructure and Mechanical Properties of Prosthesis of Forging

D. C. Rojas-Olmos¹, N. López-Perrusquia¹, M. A. Doñu-Ruiz¹, J.A. Juanico Loran¹, C. R. Torres San Miguel²

¹Universidad Politécnica Valle de México; *Grupo Ciencia e Ingeniería de Materiales*, UPVM, Tultitlán, Edo de México.

E-mail: noeperrusquia@hotmail.com

²Instituto Politécnico Nacional, SEPI-Esime, Adolfo López Mateos, Zacatenco, México D.F, C. P. 07738, México.

ABSTRACT

This work studies the change microstructural and mechanical properties of biomedical component hot forging of titanium; was assessed quantitatively and qualitatively the microstructural features obtained in this titanium biocompatible Ti6Al4V. The forging process was obtained at temperature of 950 °C, after by technical optical microscopy are obtained the microstructural characterization showing the phases present after forging. Likewise, the technical X-ray diffraction (XRD) shows the presence of the phases. Also is evaluated the hardness and modulus of elasticity by technical nanoindentation. The characterization of this material has the objective to show that the results obtained with temperature study of 950 °C. Likewise by the forging process obtained a type phases and optimal properties required for these biomedical materials.

INTRODUCTION

The industry of biomedical implants internal and external has become the last few decades in one of the most dynamic and growing annual; this trend should continue to respond to needs of the global society; this with the aim of developing implants that give a best possible quality of life [1]. The titanium alloys Ti-6Al-4V are metallic materials for biomedical applications [2-3].

The evolution of this manufacturing industry of biomedical prosthesis has been greatly enhanced by the studies of the materials used in this area of health [4]. The characterization of deformation behavior is thus essential for the optimization of hot forging processes of titanium alloys [5-6]. The manufacturing processes are an important part in the production of biomedical implants [7]. In the forging process can obtain phase α and β [8]; this have greater biocompatibility phase β types [9]. The mechanical properties of the biomedical implants, after processes of manufactures are important by changes microstructure and hot workability of the forging [10]. The decisive innovations in manufacturing of these biomedical components, by other manufacturing techniques are productive and more efficient [11]. In addition the training of biomedical implants by the manufacture of wrought iron, is a new technology.

The forging of titanium alloy blades is a difficult operation to describe quantitatively due to the changing properties of the workpiece material during forging process [12-13].

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EXPERIMENTAL

Used a lubricant for hot forging test, based glass, the press speed was 16 mm s^{-1} . The piece of forged alloy Ti6Al4V is shown in Figure 1. The chemical composition is shown in Table I. Microstructural characterization was determined by means of a metallographic microscope Olympus GX 51 along the ankle prosthesis, also by scanning electron microscopy with a JEOL 6063 L equipment and technique energy dispersive spectrometry (EDS) the distribution of alloying elements was evaluated in the biomedical component. The nanohardness with ultra-micro hardness tester Mitutoyo with maximum load of 100mN



Figure 1. Component of the Ti6Al4V alloy hot forged

Table I. Nominal chemical composition of the Ti6Al4V

Elements	(wt. %)
Al	5.5-6.5
V	3.5-4.5
Fe	0.25
C	0.08
O	0.13
N	0.05
H	0.012
Ti	Balance

RESULTS AND DISCUSSION

Figure 2 shows dark areas corresponding to α phase, while the clear zones correspond to particles of β phase dispersed in the array of α phase. Although the chemical attack employed did not reveal the contour of the grain α phase, we can infer that the grains are of type equiaxial from observation of the distribution of the particles β , which are located preferentially in these contours. This microstructure is primarily known as the type mill-annealed. In addition, it shows an optical micrograph of the longitudinal section of the bar where there is a lengthening of the grains in the direction of the forge, which coincides with the image in the horizontal axis. In the Figure 2 clear zones correspond to the grains of α and dark areas to the particles β .

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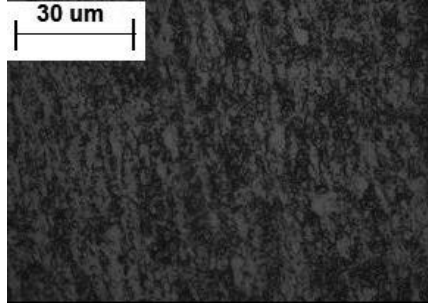


Figure 2. Microstructure of the forged alloy Ti-6Al-4V obtained by optical microscopy.

Figure 3 shows the microstructures in the majority of the sites indicate the type of structures stable α - β without defects of deformation, and some of shear bands. The material Ti-6Al-4V forging presents a type of equiaxed structure and an elongated shape unidirectional feature forged materials; in addition the bright areas are representative of the α phase, the phase darker is β . The alloying elements in this special material in the presence of vanadium in the alloy makes the biphasic ($\alpha + \beta$) improving very significantly shaping by plastic deformation of the different types of prostheses.

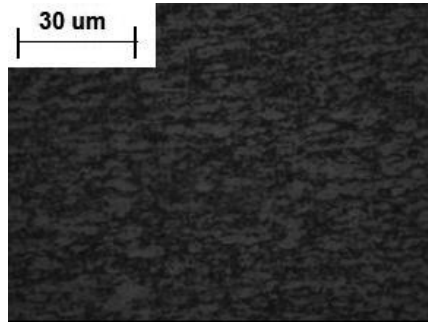


Figure 3. Micrograph obtained by optical microscopy of the Ti-6Al-4V alloy forged presenting a structure type "mill annealed".

On the other hand, this paper presents the test of nanoindentation to this material in different directions as is shown in Figure 4; in table 2 show the results the hardness and elastic modulus of the study material forged.

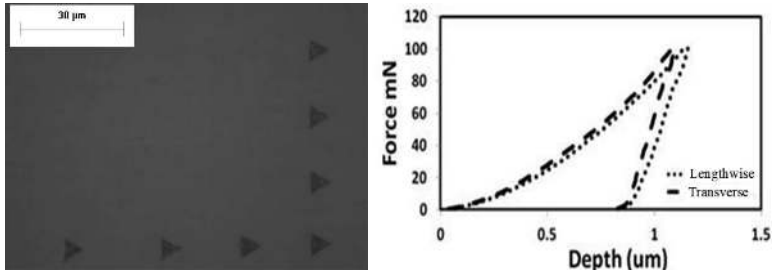


Figure 4. Nanoindentation test in different directions longitudinal and transversals to load 100 mN.

Table II. Properties of the material hot forged

	Modulus of Elasticity (GPa)		Hardness (Hv)	
	Longitudinal	Transversal	Longitudinal	Transversal
This Work	100	103	340±12.3	337.9±10.9
[14] Ti-6Al-4V	115		350.0	
[15] Ti-6Al-4V	101–110		346	
[16] Ti-6Al-4V	110		346	

The results obtained by X-ray diffraction are consistent with those found by optical microscopy in terms of the phases present in the material. In figure 5 are observed the areas of analysis on the material studied. In addition, shows figure 5 the family of levels of each of the phases which. The reflection of greater intensity for the α phase occurs at an angle of 40.42° corresponding to the (100) plane, while for the β phase occurs at an angle of 39.4° corresponding to the (110) plane, as shown in figure 5.

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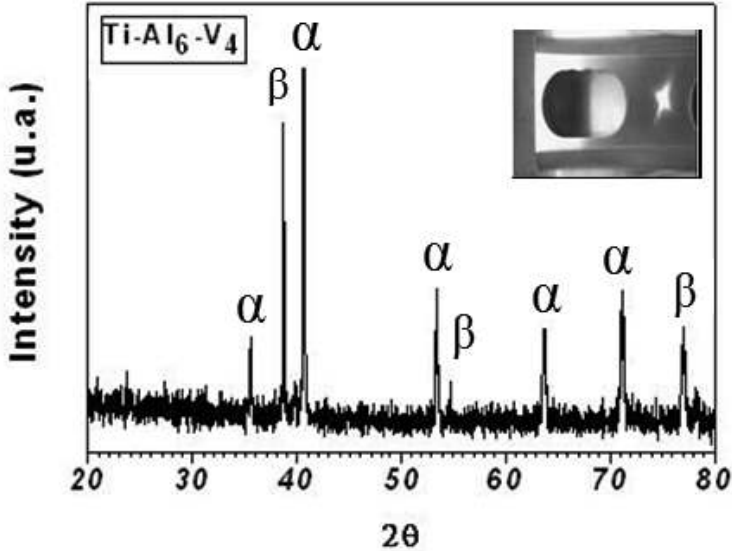


Figure 5. Areas of analysis by XRD and XRD patterns

CONCLUSIONS

The effect of hot forging on the Ti-6Al-4V alloy shows the type of the morphology and microstructure, the analysis in this study by nanoindentation shows the hardness and elastic modulus of the phases present and XRD revealed type phases in the study. Furthermore shows a microstructure bi-modal or equiaxed structure optimal for this biomedical material. The module of elasticity and hardness were obtained at different directions with the type phase β and α presented a similitude in both directions. Also observed with the forging temperature a significantly influence on the microstructure and mechanical properties. The Diffraction patterns showing the presence β phase α. With the development of engineering forging parts or biomedical components using alternative manufacturing processes, has been shown to produce an improvement on the properties of Ti-6Al-4V alloy. This study shows the results of mechanical properties obtained of forging. These results also intended to contribute to the design and manufacture of biomedical prostheses.

ACKNOWLEDGMENTS

The author acknowledge PROMEP and COMECyT of Mexico for the support by this study.

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Mater. Res. Soc. Symp. Proc. Vol. 1766 © 2015 Materials Research Society
 DOI: 10.1557/opl.2015.407

Synthesis, Characterization and Antitumor Activity of 4-Ferrocenylpyridine-3, 5-Dicarbonitrile Derivatives and Sodium Polymeric Complexes Containing Carbanionic

Ligands

E. Klimova¹, J. Sánchez¹, M. Flores¹, S. Cortez¹, T. Ramírez², A. Churakov³, M. Martínez²

¹ Facultad de Química, UNAM, México D. F., C.P.04500, México,

E- mail: eiklimova@yahoo.com.mx

² Instituto de Química, UNAM, México D. F., C.P.04500, México.

³ Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii prosp., 31, Moscow 119991, Russia.

ABSTRACT

The reactions of 2-cyano-3-ferrocenylacrylonitrile with malononitrile in a ROH/H₂O medium in the presence of Na₂CO₃ afforded 6-alkoxy-2-amino-4-ferrocenylpyridine-3,5-dicarbonitriles, 6-alkoxy-2-amino-4-ferrocenyl-3-ferrocenyl-methyl-3,4-dihydropyridine-3,5-dicarbonitriles and Na⁺ polymeric complexes: {[Na⁺(2-ferrocenyl(tetracyano)propenyl)⁻L]_∞} and [Na⁺(2-amino-3,5-dicyano-4-ferrocenyl-6-pyridyl-dicyanomethyl)⁻L]_∞ where L = ethanol, methanol. Complexes with L = acetonitrile (c), dimethylformamide (d), acetone (e), ethyl acetate (f) were prepared by recrystallization. The structures of the compounds 4b and Na⁺ polymeric complexes 5c and 6d, e were established by the spectroscopic data and X-ray diffraction analysis. Two compounds 3a and 4a were tested *in vitro* against six human tumor cell lines U-251, PC-3, K-562, HCT-15, MCF-7 and SKLU-1 to assess their *in vitro* antitumor activity. The results suggest biological specificity towards PC-3, K-562 and HCT-15 cells for compound 3a, and towards PC-3 cell for compound 4a at doses 50 μM, which are lower than Cisplatin IC₅₀'s in the three cell lines.

INTRODUCTION

Recently, the interest in the chemistry of compounds of the ferrocene series has been increased due to their possible practical applications. Data on the industrial use of the ferrocene derivatives available from the patent literature [1, 2] reflect mainly their employment in military-industrial establishment and rocket technologies.

Publications demonstrating the use of ferrocene derivatives in nonlinear optics devices, chemistry of polymeric materials, synthetic organic chemistry (asymmetric synthesis) [3, 4], medicinal chemistry [5] supramolecular chemistry [6], chemo- and biosensors [7], materials science [8, 9], etc.

The ferrocene molecule itself is an energy rich structure. Therefore, studies on compounds comprising other energy rich fragments, such as ene, diene, and polyene chains, fused carbo- and heterocyclic systems, etc., in addition to the ferrocene moiety, are of special interest [10]. The incorporation of one or two iron-containing ferrocene substituents into a heterocyclic molecule will enlarge the spectrum of valuable characteristics. In particular, ferrocenyl-substituted pyridines have been extensively studied as ligands, in the synthesis of non-linear optical materials, etc. [11-13]. However, their biological activities have not hitherto been studied. Various methods to prepare ferrocene-containing pyridines have been reported [14]. The interest in pyridine compounds bearing ferrocenyl substituents in the molecules can be traced back to the discovery of ferrocene. In particular, biological activities of many nitrogen heterocycles, such as quinuclidines, pyrazolines, pyrazoles, pyrimidines, tetrahydropyridazines, bearing ferrocenyl substituents, have been reported [5]. It may be expected that ferrocenylpyridines and cyano(ferrocenyl)pyridines will also prove valuable, because they possess diverse biological activity, find use as potential bio-receptor ligands [15] new drugs [16] and significant intermediates for the synthesis of important materials [17]. For these reasons, development of new compounds containing cyano and ferrocenyl groups in the pyridines is strongly desired. In the present work, we report results from our investigations into reactions of the condensation of 2-cyano-3-ferrocenylacrylonitrile 1 with malononitrile 2 and of the tandem-transformations of 1 in alcohols/aqueous medium in the presence of bases and nucleophiles.

EXPERIMENTAL

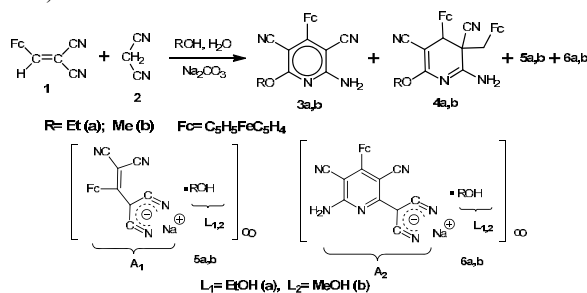
All the solvents were dried according to standard procedures and were freshly distilled before use. Column chromatography was carried out on alumina (Brockmann activity III). The ^1H and ^{13}C NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) for solutions in CDCl_3 with Me_4Si as the internal standard. The IR spectra were measured with an FTIR spectrophotometer (Spectrum RXI Perkin - Elmer instruments) using KBr pellets. The mass spectra were obtained on a Varian MAT CH-6 instrument (EI MS, 70 eV). Elementary Analysensysteme LECO CHNS-900 was used for elemental analyses. The unit cell parameters and the X-ray diffraction intensities of 4b, 5c, 6d and 6e were recorded on a Gemini (detector Atlas CCD, Cryojet N_2) diffractometer. The structure of compounds 4b, 5c, 6d and 6e were solved by the direct method (SHELXS-97 [18]) and refined using full-matrix least-squares on F^2 . 2-Cyano-3-ferrocenylacrylonitrile 1 was prepared by condensation of ferrocenecarbaldehyde with malononitrile in benzene in the presence of piperidinium acetate.

Reaction of 2-cyano-3-ferrocenylacrylonitrile 1 with malononitrile 2 in the presence of Na_2CO_3 : Exp. 1: a mixture of compound 1 (1.13 g, 5.0 mmol), malononitrile 2 (0.4 g, 6.0 mmol), ethanol or methanol or (100 mL), H_2O (10 mL) and Na_2CO_3 (0.5 g, 5.0 mmol) was stirred and refluxed for 8 h. The solvents were removed *in vacuo* and the residue was dissolved in dichloromethane (50 mL). The solution was mixed with Al_2O_3 (activity III, 20 g) and the solvent was evaporated in air. This sorbent was applied onto a column with Al_2O_3 (the height of alumina is *ca.* 20 cm) and the reaction products were eluted from the column first with petroleum ether, then with a 2:1 hexane-dichloromethane to give compounds 3a,b, 4a,b, polymeric compounds 5a,b (with 6:1 dichloromethane – methanol) and 6a,b (eluent 1:2:1 dichloromethane - methanol – water) [19,20].

[More Information](#)

RESULTS AND DISCUSSION

All experiments were carried out using 2-cyano-3-ferrocenylacrylonitrile **1** with malononitrile **2** [$\sim 1:1.2$ (exp. 1), $\sim 1:3$ (exp. 2), respectively] in EtOH/H₂O or MeOH/H₂O medium in the presence of Na₂CO₃ by refluxed (Table 1). We found that following competitive processes occur upon this reaction: formation of 6-alkoxy-2-amino-4-ferrocenylpyridine-3,5-dicarbonitriles **3a,b** multi-component condensation, cyclodimers **4a,b** multi-component cyclodimerization, and formation of the Na⁺ polymeric complexes: {[Na⁺(2-ferrocenyl(tetracyano)propenyl)L]_∞}⁺ **5a,b** and [Na⁺(2-amino-3,5-dicyano-4-ferrocenyl-6-pyridyl-dicyanomethyl)L]_∞ **6a,b**, where L = ethanol, methanol (Scheme 1).



Scheme 1 Multicomponent competitive reactions of 2-cyano-3-ferrocenylacrylonitrile with malononitrile.

Table I. Reactions of 2-cyano-3-ferrocenylacrylonitrile **1** with malonitrile **2** in EtOH (a) or MeOH (b) in the presence of Na₂CO₃

Exp 1: FcCH=C(CN) ₂ + CH ₂ (CN) ₂				Exp 2: FcCH=C(CN) ₂ + CH ₂ (CN) ₂			
5 mmol		6 mmol		5 mmol		15 mmol	
EtOH ~ 70°C		MeOH ~ 60°C		EtOH ~ 70°C		MeOH ~ 60°C	
No	Yield (%)	No	Yield (%)	No	Yield (%)	No	Yield (%)
3a	48	3b	52	3a	6	3b	5
4a	19	4b	18	4a	6	4b	7
5a	7	5b	5	5a	21	5b	20
6a	6	6b	6	6a	45	6b	51

[More Information](#)

All products were isolated by column chromatography on alumina: compounds 3a,b and 4a,b with eluent 2:1 hexane - dichloromethane, 5a,b with eluent 6:1 dichloromethane - methanol and 6a,b with eluent 1:2:1 dichloromethane - methanol - water, and their structures were characterized by IR and NMR spectroscopy, mass spectrometry, and elemental analysis. The molecular structure of compound 4b was determined by X-ray diffraction analysis of their single crystals. The general view of molecule 4b is shown in Fig. 1. Key elements of the molecules 4b is the central six-membered ring with one nitrogen atom in the half-chair conformation. The N(1)-C(23) (for 4b) bond lengths is equal to $d = 1.319(3)$ Å. The ferrocenyl and ferrocenylmethyl substituents at C-4 and C-5 of 4b are *trans* oriented relative to the 6-membered cycle.

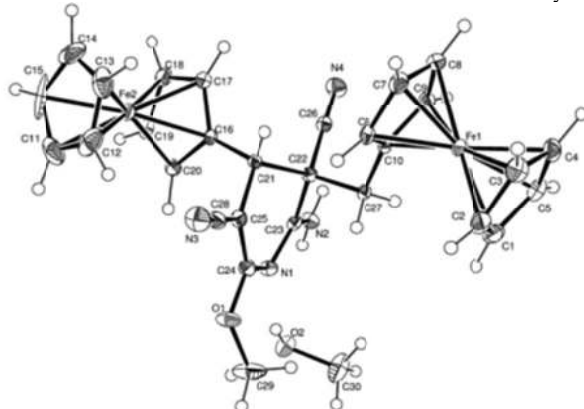


Figure 1 .The Crystal structure of 4b. CCDC- 878739.

Compounds 5a, b and 6a, b are red powders. Their structures were established by IR, ^1H and ^{13}C NMR spectroscopy and mass spectrometry. The IR spectra of compounds 5a, b and 6a, b contain bands at $2170\text{--}2225\text{ cm}^{-1}$, which are characteristic of the cyano groups. The ^1H NMR spectra of these compounds contain characteristic signals for one ferrocenyl substituent and signals for one molecule of ethanol or methanol. In addition, the spectra of compounds 6a and 6b contains also signals for protons of the NH_2 groups. Data from ^{13}C NMR spectra of 5a, b and 6a, b corroborate the presence in each compound of one ferrocenyl fragment, one methyl group, four cyano substituents, and they also contain signals of one $\text{C}_{\text{ipso}}\text{Fc}$ carbon atoms, three and six quaternary carbon atoms, respectively. Mass-spectra of compounds 5a, b and 6a, b showed the signals corresponding to molecular ions $[\text{M}]^+$ ($m/z = 325$ and 391 , respectively), $[\text{M}+\text{Na}]^+$ ($m/z = 348$ and 414 , respectively), $[\text{M}+\text{Na}+\text{CH}_3\text{CH}_2\text{OH}]^+$ ($m/z = 394$ and 460 , respectively) and $[\text{M}+\text{Na}+\text{CH}_3\text{OH}]^+$ ($m/z = 389$ and 446 , respectively). On this basis, we supposed that compounds 5a,b and 6a,b may represent the sodium polymeric complexes containing carbanionic 2-ferroceny(tetracyano)propene and 3,5-dicyano-6-dicyanomethyl-(ferrocenyl)pyridine, respectively, and ethanol or methanol ligands (Scheme 1). Further, we observed that upon recrystallization of compounds 5a from CH_3CN , acetonitrile substitutes ethanol forming a new crystalline product 5c. Similarly, recrystallization of 6a from CH_3CN , $(\text{CH}_3)_2\text{NCHO}$, $(\text{CH}_3)_2\text{CO}$ and