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DESIGN AND DEVELOPMENT OF TITANIUM-BASED COPPER-BEARING ALLOY IMPLANT FOR BIOMEDICAL APPLICATION

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ABSTRACT

There is a serious need for indigenous manufacture of titanium-based alloys for small scale production of implants. Incessant accidents on Nigeria's poor roads lead to permanent injury or loss of limbs. Replacements of these limbs are therefore necessary for the poor victims. However, the high costs of treatment or replacement of these body parts have led to permanent incapacitation. This is ultimately due to the unavailability of these materials locally, in Nigeria. In this work, a potential antibacterial Ti-3.5Cu-based alloy was designed and developed, with commercially pure titanium (cp-Ti) used as control. The novel Cu-bearing Ti-3.5Cu alloy with optimum mechanical properties and attractive physical properties was designed and fabricated. Bond order (Bo) and metal d-orbital (Md) method was used in designing the alloys. Data values obtained from this hypothesis were used to predict the properties of the different alloys. Hot forging of the billet was done in temperature range 750–765^{o}C (to 75% deformation), followed by hot rolling at about 800–807^{o}C (deformed by 94.24%) and finally heat-treating above their beta transition temperatures (BTT). Results for Bo-Md design analysis, microstructural, mechanical and physical properties show promising basis for development of implant for orthopaedic application.

Keywords: Ti-3.5Cu Alloy, Mechanical Properties, Implant, Locally-Manufactured, Physical Properties.

I. INTRODUCTION

Metallic implants represent a significant component of biomedical treatments involving bone fracture, reconstruction, and replacement and have significantly improved the quality of life for patients in recent years [1]. In fact, of biomaterial implants, metallic implants represent a major class of components (particularly for orthopedic fracture treatment and joint replacement) and have been largely successful since the development of advanced titanium (Ti), cobalt (Co), and stainless-steel alloys [2]. Further, a whole new generation of three-dimensional printed Ti orthopedic implant components, directly modeled on a patient's own bone structure, is on the horizon. A recent estimate for the 2010 global annual market for orthopedic implant devices was about $30 billion, with an annual growth rate of 8.2%, which represents an overall market value upward of $50 billion by 2018 [3].

The healthcare system in West Africa is still relatively underdeveloped, and the markets for specialized medical services remain constrained [4]. The underlying challenge has been a lack of funding. However significant strides are being made, especially in the larger countries such as Nigeria, Malaysia and South Africa, with governments demonstrating greater commitment towards development of healthcare infrastructure. In recent years, the Nigerian government has consistently increased its budget allocations towards the upgrading of orthopaedic hospitals. The orthopaedic environment in Nigeria is transforming, and previously unavailable surgical procedures have been introduced at major orthopaedic institutions. The threat posed by overseas competition is diminishing as an increasing number of Nigerians is now undergoing operations locally rather than abroad. These positive developments have encouraged Nigerian surgeons, many of whom have now chosen to stay, bucking the traditional trend of emigrating to overseas destinations.

Nigerians who can afford it have resorted to medical tourism especially for surgeries (mostly orthopaedic and cancer), cardiology, neurology and management of cancers [5]. Nigerians spent an estimated USD260 million on medical bills in India alone in 2012 and 40% of all visas to India were for medical reasons. The Nigerian Medical Association (NMA) estimates that Nigerians spend USD500 million to USD1 billion on medical tourism per year. Besides India, other major medical tourism destinations for Nigerians are Turkey, South Africa, Saudi Arabia, USA, UK and Germany. Key services sought are oncology, orthopaedic surgeries and cardiology [5, 6].

Though tertiary care institutions are funded mostly by the federal government, an analysis of the federal annual budget from 2010 to 2014 shows that, on average, over 60% of the federal annual health budget goes to personnel costs, leaving little for infrastructural development, expansion, acquisition of new equipment and scaling up of services [7]. This has resulted in run down tertiary hospitals, a key contributor to the huge medical tourism mentioned earlier. To overcome the budgetary constraints to capital investments in the tertiary hospitals, the Federal government has over the years, adopted a "special projects" approach to fund major upgrade [8]. Funds are earmarked for these projects outside the standard budget and sometimes funding is also sourced from partners.

This work is therefore geared towards solving the problem of a virtually non-existent locally produced implant materials in Nigeria. Titanium-copper (Ti-Cu) bearing biomedical alloy was developed in our local workshop and laboratory at the Federal Polytechnic, Offa and at another facility in Kwara State, Nigeria. The raw materials were imported from Shenyang, China through an existing arrangement made by the principal investigator. The actual fabrication, pyrometallurgical processing and mechanical characterization were done at our facilities while further sophisticated analyses were done at the IMR facility in Shenyang. The entire procedures done locally will therefore create a robust avenue for more local content production processes. Design analysis using Bo-Md method, mechanical properties, compositional analysis were carried out to form the preliminary of the investigation of the alloys for use as implant. Commercially pure titanium (cp-Ti) was used as the control while the 3.5 wt. % Cu alloy was the target specimen for use as an antibacterial implant.

II. METHODOLOGY

2.0 Experimental Design, Materials and Methods

2.1 Samples preparation

The city where the raw materials were obtained is Shenyang, which ranges in latitude from 41° 11' to 43° 02' N and in longitude from 122° 25' to 123° 48' E, located in the central part of Liaoning province of Northeastern China. The designed Ti alloys, Ti-3.5Cu were produced in a 25kg vacuum consumable furnace that is usually used for melting titanium alloys. Titanium sponges (particle size 3–12.7mm), 99.99% purity, was supplied by Chaoyang Jinda Industry of China. Cu pellets (ø 2 x 10 mm), 99.99% purity, was supplied by Copper (Shenyang) Technology Co., Ltd. Ti element was used as control. Prior to melting, pre-mixed samples were weighed on a clean balance, and then the mixtures were densified into stocks of solid blocks in a hydraulic press chamber [9]. The stocks were then loaded into an ethanol-cleaned, water-cooled copper crucible and melted at least thrice times to ensure complete homogeneity.

2.2 Melting operation

In batches, the samples which served as the electrode were loaded into the 25kg vacuum consumable furnace. The temperature of the furnace was about 2,000°C and the vacuum order was set to 30 mbar, with current of 2000A and operating voltage range of 28.4–31.3V. The water-cooled copper mould automatically rotated while the melting operation continued to ensure a thorough mix. The melting operation lasted for 5-6 minutes for each alloy. To ensure complete homogenization, re-melting was done thrice [10].

2.3 Hot forging

The obtained ingots from the copper moulds were 100 mm diameter each. They were allowed enough time to cool then transferred to another argon-purged furnace for pre-heating up to 765°C. The hot blank was then transferred to a pneumatically controlled open-die forge, where compressive localized forces were applied [11]. The maximum pressure of the forge is 16,000 tonnes with 75% uniform deformation achieved.

2.4 Hot rolling

The 50mm blanks obtained from hot-forging were further passed through a three-layer rolling mills to achieve rods diameter of 12mm, about 95% deformation [12]. Prior to rolling, the blanks were again preheated to a temperature of 807°C.

2.5 Heat treatment

Heating and then furnace cooling at 20°C/s above each alloy BTT point for 7200 s was carried out [13]. This was to suitably allow for precipitation of intermetallic compounds in the alloys. The average heating rate was kept at 5°C/min.

2.6 Electron Discharge Machining (EDM) cutting

The various 12 mm rods were labeled accordingly and EDM cutting was used to slice them into the following dimensions for the various tests: (a) ø 10 x 2 mm (and then ground with SiC up to 2000 grit paper for hardness, and density tests); (b) ø M10 x 5 mm at strain rate of 0.017 s^{-1} (turned on a lathe, according to GB/T 228.1-2010, which is equivalent to ISO 6892-1: 2009, for tensile tests: i.e., yield and tensile strengths) [14.15]; (c) ø 10 x 80 mm (for Young's modulus test) [9, 16].

2.7 Density measurement

Buoyancy method of density determination was employed using a Dual Range Mettler Toledo XS105 (Switzerland). The method entailed obtaining the weights of the samples in air (23.9°C) and water with their corresponding densities [2, 12, 17].

2.8 Young's modulus measurement

Samples were submitted for the resonance frequency technique, a dynamic measurement form of testing. For the sample, cylindrical in shape, ø 10 x 80 mm, the value of E was obtained as follow:

$$E = 1.6067 \times 10^{-9} (m \times {f^2}_f) \cdot \left\{\frac{l^3}{d^4}\right\} . T_1 \qquad (1)\ [18]$$

where E is the Young's modulus (GPa), m is sample mass (g), l is length (mm), d is diameter (mm), f_f is the intrinsic bending resonance frequency (Hz) and T_1 is the correction coefficient. This was performed according to the test standard GB/T 22315-2008 (Chinese standard) at room temperature (about 24°C). The test equipment, RFDA HTVP 1750-C manufactured by IMCE Company, Belgium, was used to take measurements three times each. Average data values were obtained after the experiment was performed in quintuplicate.

2.9 Hardness test

A microhardness tester, supplied by Shanghai Yan-Run Optical Machine Technology Co. Ltd., was used to test for the samples' hardness. The HRV data values were obtained using a force, F= 2.9420N, and a time, t= 10 secs [19]. Prior to testing, the samples were successively ground using silicon carbide (SiC) abrasive paper of grades 180, 400, 600, 800, 1,000 and 2,000 grit on a motor-controlled rotary machine. The average data were obtained for n=5.

2.10 Chemical analysis

An inductively coupled plasma-mass spectrometry (ICP-MS), manufactured by PerkinElmer, model Optima 7300DV, was employed in determining the alloys chemical compositions. The chips obtained in lathe machining were further ground to fine particles, cleaned in ethanol and then fan-dried for analysis of the main elements. Other gaseous substances that may be present were also analyzed with TCH600 O/N/H analyzer and sample specifications of ø 4 x 50 mm.

III. RESULTS AND DISCUSSION

The results obtained presents the information about the chemical compositions, tensile strength, yield strength, hardness value, Young's modulus, hardness values and elongation for the Ti-3.5Cu alloy and the cp-Ti as control.

Table 1 shows the data for the bond order (Bo) and metal d-orbital (Md) design values that describe the type of alloys to be obtained for the Cu-bearing alloy and the cp-Ti element, respectively. Our design was to ensure a series of alloys that would possess the structures and properties of an α+β-phase without any trial-and-error experiments. These Bo and Md values suggest that a comparatively low-value Cu (3.5 wt.%) will achieve this target. We have obtained 2.52 and 2.23 and 2.73 and 2.68 respectively as the compositional averages for our Ti-3.5Cu and cp-Ti alloys, respectively. These compositional averages, now represented as $\overline{Bo}$ and $\overline{Md}$, were obtained as shown in (1) and (2).

$$\overline{Bo} = \Sigma X_i \,.\, (Bo)_i \qquad (1)$$

$$\overline{Md} = \Sigma X_i \,.\, (Md)_i \qquad (2)\ [19]$$

Table 1: Bo and Md values for various alloying elements in bcc Ti

Element (components $_i$)	Bo	Md (eV)
Ti	2.790	2.447
Cu	2.114	0.567

where X_i is the weight fraction of the components in the alloy, $(Bo)_i$ and $(Md)_i$ are the respective values for components $_i$. The summation extends over the components $_i$ = 1, 2, … n [19].

Alloy samples were of very high purity (at least 99.9%) as shown in the chemical composition analysis (Table 2) obtained using ICP-MS (Perkin Elmer, Optima 7300DV) and TCH600 O/N/H analyzer to confirm the non-significant interstitial elements showing small concentrations. Cp-Ti was used as control.

Table 2: Chemical composition of the Ti-3.5Cu and cp-Ti alloys

Element	Cp-Ti (wt. %)	Ti-3.5Cu (wt. %)
Ti	Bal.	Bal.
Cu	0.01	3.48
Fe	0.04	0.06
C	0.05	0.04
O	0.07	0.06
N	0.004	0.007
H	0.003	0.002

The data for physical properties are presented in Table 3 while those of mechanical properties are shown in Table 4 after the alloys have been melted and homogenized at about 1675^{o}C, hot-forged at about 765^{o}C (from a Ø100 mm billet to Ø50 mm round bar), hot-rolled at about 807^oC (from Ø50 mm to Ø12 mm rod) and then heat-treated at slightly above their BTT. In all cases, Cu additions led to increased physical and mechanical properties. As shown in Table 3, we obtained the values of densities and Young's modulus to be within acceptable standards for Ti alloys used as implants. In Table 4, it would also be seen that the elongation shows that Cu tended to increase the alloys' plasticity, and the addition significantly improved the alloys' ductility, attaining over 96% increment over the unalloyed sample. That is, Ti-3.5Cu alloy presented better ductility of over 30%, even far higher than the cp-Ti. In addition, the hardness values with Cu addition was better than that of cp-Ti achieving as high as 369 HRV. Moreover, the tensile strength, yield strength and hardness increased drastically by 16.7%, 23.4% and 96.1% respectively between Ti-3.5Cu and cp-Ti alloys. On the overall, Ti-3.5Cu displayed the best combination of mechanical properties.

Table 3: Values of density and Young's modulus for the Ti-3.5Cu and cp-Ti alloys

Alloys	Density (g/cm^3)	Young's modulus (GPa)
Ti-3.5Cu	4.86	110
Cp-Ti	4.81	108

Table 4: Mechanical properties for the Ti-3.5Cu and the cp-Ti alloys

Alloys	Yield strength (MPa)	Tensile Strength (MPa)	Hardness (HRV)	Elongation (%)
Ti-3.5Cu	586±6.3	748±6.8	369±4.8	30.2±1.8
Cp-Ti	502±2.8	606±6.1	248±1.6	15.4±0.3

Figs. 1 (a) and (b) show the microstructures obtained from an optical microscope of both the cp-Ti and the Cu-bearing Ti alloy. It can be seen that the appearances of the two samples are distinctively different. While the cp-

Ti showed a light appearance with fine microstructures, that of the Ti-3.5Cu displayed a combination of light and dark morphology, both uniformly dispersed in each other. This could be said to be as a result of the Cu-addition to the Ti-3.5Cu alloy [20]. Hence, adopting a α+β biphasic microstructure. As already discovered in our previous works, a monophasic structure such as Cp-Ti yields a comparatively lesser strengthening effect compared to those having alloying elements that evoke the nucleation of an additional phase or precipitation of particles, like the 3.5Cu. This explains why the cu-bearing alloys possessed better mechanical properties than the cp-Ti [10, 21]. In addition, the even distribution of the additional phase (β) aids the improved ductility of the Ti-3.5Cu alloy which tends to act as barrier to grain boundaries, thus drastically increasing the percentage elongation of the Cu-bearing alloy [22-25].

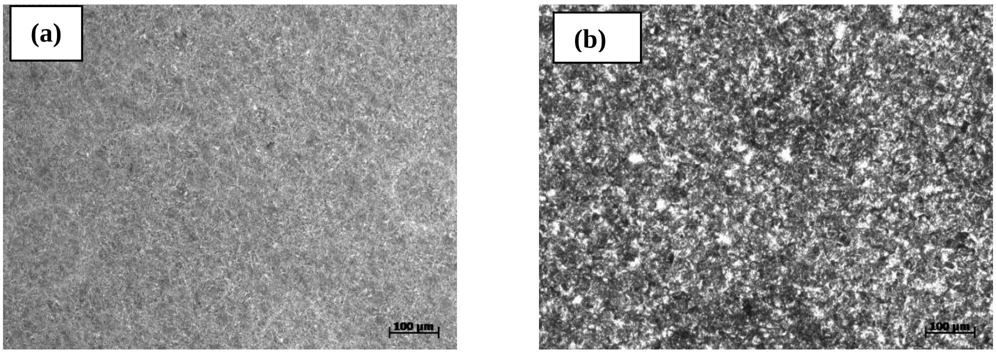

Figure 1: Optical microstructures of the (a) cp-Ti and(b) Ti-3.5Cu alloy.

IV. CONCLUSION

Based on the analysis of the designed and fabricated alloys, the following conclusions can be drawn:

1. The hypothesis tool, Bo-Md data could be used to obtain the alternative scientific approach to designing alloys rather than the traditional trial-and-error method.
2. The values obtained for tensile strength, yield strength, hardness, Young's modulus, elongation and relative density for the Ti-3.5Cu alloy, being those of mechanical and physical properties of the new potential implant alloy suggest that the alloy is a good candidate for use as orthopaedic implants.
3. The thermomechanical process used in the production process of the alloy aided in blending the Cu well to the base element, thus forming an even distribution of the α and β phases within each other. This also contributed to the improved alloy's ductility.

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