Aluminum- and Vanadium-free Titanium Alloys for Medical Applications

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Abstract

CP-Ti, Ti 6Al 4V (ELI), and Ti 6Al 7Nb are often used for manufacturing osteosynthesis products or implants. However, researches have revealed that Al and V can have detrimental effects on the human body. Therefore, several Al- and V-free near- α and ($\alpha+\beta$) titanium alloys have been developed on the basis of CP-Ti Grade 4⁺ (Ti 0.4O 0.5Fe 0.08C). They should possess similar or better mechanical properties than Ti 6Al 4V (ELI) combined with an improved biocompatibility and good corrosion resistance. O, C, Fe, Au, Si, Nb, or Mo have been used as alloying elements, which are either already present in the human body or are biocompatible. Several of the studied alloys show a strength and ductility fulfilling the requirements of Ti 6Al 4V ELI as specified in ASTM F136. For instance, Ti 0.44O 0.5Fe 0.08C 2.0Mo exhibits a YTS of approx. 1005 MPa, an UTS of approx. 1015 MPa, and an elongation at rupture of at least 17%. Therefore, one or more of the studied alloys are promising candidates for replacing Ti 6Al 4V ELI in osteosynthesis and implant applications.

1. Introduction

Titanium alloys combine good mechanical properties with biocompatibility and corrosion resistance and are, therefore, very well suited for medical applications [1-3]. For instance, CP-Ti and Ti 6Al 4V are often used for manufacturing implants [2]. Since V is toxic and can adversely affect the human body [2-4], Ti 6Al 7Nb was designed on the basis of Ti 6Al 4V to tackle possible negative health effects of this alloying element [1, 5]. Al is also a known toxic element [3, 4] and might cause Alzheimer's disease [2]. Additionally, Mandriota et al. [6] found out experimentally in mouse cancer models that aluminum chloride can cause breast cancer. Consequently, the high Al content of Ti 6Al 4V (ELI) and of Ti 6Al 7Nb is (still) of concern and long term negative health effects cannot be excluded per se.

Therefore, in the present study, several Al- and V-free titanium alloys for osteosynthesis and implant applications have been developed. They are all based on CP-Ti Grade 4⁺ (CP-Ti Grade 4 with maximum allowed contents of O, Fe, and C according to ASTM F67 - Ti 0.4O 0.5Fe 0.08C), which was already discussed in [7], and contain Mo, Au, Si or Nb as additional solid solution strengthener. O, C, Fe, and Mo are essential for the human body [8], whereas Au, Si, and Nb are biocompatible [3]. Table 1 lists the chemical composition of some of the studied alloys which are discussed in this paper. Corrosion experiments show that they (Ti 0.44O 0.08C 0.5Fe 0.4Si 0.1Au not yet tested) possess a better corrosion resistance than Ti 6Al 4V ELI. Due to the exclusion of potential critical elements, it is suspected that these alloys show a better biocompatibility than Ti 6Al 4V (ELI) combined with similar or better mechanical properties.

Table 1: Chemical composition of the studied alloys (differences between the alloys are printed in bold)

Ti 0.42O 0.08C 0.5Fe 0.4Si	Ti 0.44O 0.08C 0.5Fe 0.4Si
Ti 0.40O 0.08C 0.5Fe 2.0Mo	Ti 0.44O 0.08C 0.5Fe 2.0Mo
Ti 0.40O 0.08C 0.5Fe 2.0Nb	Ti 0.44O 0.08C 0.5Fe 2.0Nb
Ti 0.40O 0.08C 0.5Fe 0.3Si 0.1Au	Ti 0.44O 0.08C 0.5Fe 0.4Si 0.1Au

2. Methods

Alloy and specimen production

Laboratory-size specimens have been produced by plasma beam cold hearth melting. CP-Ti Grade 4, CP-Ti Grade 1S foil, graphite powder, TiO₂ powder, gold, iron, niobium, molybdenum, and silicon chips were weighed out according to the required chemical composition. For the melting process, the chamber was evacuated and filled with Argon up to a pressure

of 600 mbar. After three times remelting, the ingot was poured into round copper molds to cast bars (13.2 mm x approx. 80 mm) for subsequent rotary swaging. In order to release residual stresses, the resulting bars have been stress relief annealed in argon atmosphere at 700°C for 90 min followed by furnace cooling.

To achieve a recrystallized, globular microstructure the cast and annealed bars were rotary swaged in four steps to a final diameter of 10 mm with a diameter reduction of 0.2 mm in the first and 1 mm in each of the last three steps. Prior to deformation, the bars were heated in a standard air tube furnace at 930°C for 22 min. Between each step, they were reheated at the same temperature for 5 min. After the final pass, the bars were straightened and air cooled and finally recrystallization annealed at 705°C for 120 min followed by air cooling.

In order to compare the mechanical properties of the alloys with CP-Ti Grade 4, Ti 6Al 4V ELI, and Ti 0.40 0.5Fe 0.08C, the latter have been produced in a very similar way, described in [9].

Two alloys (Ti 0.40 0.5Fe 0.08C 0.3Si 0.1Au and Ti 0.440 0.5Fe 0.08C 0.4Si 0.1Au) were produced in larger quantities at Access in Aachen, Germany (the former alloy, approx. 6 kg) and VACUCAST in Berlin, Germany (the latter alloy, approx. 22 kg) via cold crucible induction melting followed by vacuum casting. The conical bars which have been cast by Access had a minimum diameter of 40 mm and a length of approx. 400 mm. Some of them were first rotary swaged at TU Darmstadt in Darmstadt, Germany, to a diameter of 25 mm in one step, sectioned into four parts, and finally rotary swaged to a diameter of approx. 15 mm at Bremen University in Bremen, Germany, in one step. Prior to each deformation process, they had been annealed at 950°C for 60 min. Recrystallization annealing had been done at 800°C for 60 min with subsequent air cooling.

The bars which have been cast by VACUCAST had a diameter of approx. 38 mm and a length of approx. 360 mm. After further processing by VACUCAST, a section of one bar has been annealed at 950°C for 49 min and subsequently rolled to a thickness of approx. 8.2 mm in 16 steps followed by air cooling. Between each pass, the section had been annealed at 950°C for 10 min. After this first deformation process, a two-stage annealing treatment (1025°C/10 min/water quenching + 900°C/1.5h/air cooling) with the first step above β -transus has been done in order to achieve a fine (α + β)-microstructure of the plate through a complete decomposition of martensite. Afterwards, the plate has been rolled to a final thickness of approx. 3.9 mm in several steps with a thickness reduction of approx. 0.2 mm during each pass. Prior to deformation, the plate has been annealed at approx. 300°C for 20 min and reheated at the same temperature for 4 min after each pass. After the last step, the plate has been water quenched to prevent recovery. The final recrystallization heat treatment has been done at 800°C with a holding time between 15 min and 2 h followed by air cooling to study the recrystallization behavior.

Microstructure Investigations and phase determination

The microstructure of the alloys has been analyzed in cross section or along the longitudinal axis. To do so, small specimens were cut, warm embedded into EpoMet[®] and Bakelit compound, and subsequently ground, polished, and etched. Microstructure investigations have been performed using optical and scanning electron microscopes. Additionally, element partitioning has been studied through energy dispersive x-ray spectroscopy (EDS). Phase analysis has been done by means of x-ray diffraction in Bragg-Brentano-setup or in parallel beam geometry (the latter with primary monochromator). The resulting diffraction pattern has been analyzed with CMPR [10] software and PDF2 database (release 2005).

Mechanical testing

The hardness of the embedded and polished specimens was determined through automated Vickers hardness tests (HV 10, 5 indentations). Additionally, tensile tests compliant with DIN EN ISO 6892-1, procedure B, have been carried out at room temperature with two round tensile specimens (DIN 50125 - B 5 x 25) for each alloy and subsequent assessment of the fracture surface. Furthermore, stress-controlled fatigue tests have been carried out at Ti 0.40 0.5Fe 0.08C 0.3Si 0.1Au (produced in larger quantities). The specimens were hourglass-shaped according to ASTM E 466, had a metric fine thread of diameter 9 mm, and were ground with P2500 SiC paper in axial and transverse directions after machining to remove scratches. The tests had been carried out under a frequency of 8 Hz, an R value of approx. 0.01, and were stopped after 5×10^6 cycles in case no failure occurred.

3. Results and discussion

Microstructure and phase determination

In the as-cast and stress-relief annealed state all alloys exhibit a lamellar (α + β) microstructure. After rotary swaging and recrystallization, the microstructure of the Si- and Nb-containing alloys mainly consists of lamellae, see Figure 1, left, which exemplarily shows the microstructure of Ti 0.420 0.08C 0.5Fe 0.4Si. However, several grain boundaries in the lamellar structures or α_p -grains between the lamellae indicate that recrystallization occurred. The Si-containing alloys already exhibit a significant amount of β -phase. The corresponding grains have a size of several hundred nanometers up to a few micrometers. Local EDS measurements show that Fe is partly enriched along α -lamellae grain boundaries, which is matching to the fact that Fe is a β -stabilizer and tends to enrich in the β -Phase due to element partitioning [1]. In terms of the

Nb and Mo containing alloys, EDS analysis shows an enrichment of Nb and Mo in β -grains. Both Mo-containing alloys exhibited a significant higher degree of broken laths and more α_p -grains, see Figure 1, right, which exemplarily shows the microstructure of Ti 0.44O 0.08C 0.5Fe 2.0Mo. Accordingly, these alloys exhibit a higher degree of recrystallization. Nevertheless, residual grain boundary- α is still visible. This as well as the residual lamellar structures shows that the degree of deformation during rotary swaging was not high enough to break the laths completely. Furthermore, the repeated annealing between each pass during rotary swaging could have led to recovery of the microstructure, which – as a result – limits the degree of recrystallization. Therefore, a complete recrystallization of the samples could not be reached in laboratory conditions.

Figure 1: Microstructure of Ti 0.42O 0.08C 0.5Fe 0.4Si (left) and of Ti 0.44O 0.08C 0.5Fe 2.0Mo (right) after recrystallization (longitudinal direction)

The microstructure of Ti 0.4O 0.5Fe 0.08C 0.3Si 0.1Au (produced in larger quantities) after rotary swaging and recrystallization consists of globular α_p -grains. Local EDS analysis shows an Fe-enrichment in grains alongside of α -grains, indicating the presence of a small amount of β -phase.

Figure 2, left, shows the microstructure of Ti 0.44O 0.5Fe 0.08C 0.4Si 0.1Au along the longitudinal direction (differential interference contrast, DIC) after a recrystallization treatment at 800°C for 2 h with subsequent air cooling. It can be seen that this heat treatment led to a fine recrystallized, globular microstructure with an average grain size of approx. 11 μ m. Nevertheless, some residual lamellar structures are still present as well as larger α_p -grains along prior β -grain boundaries. Generally, the β -grains have a size of a few micrometers. Although the recrystallization temperature is low with respect to β -transus (1000°C – 1025°C), the overall amount of β -phase in the alloy is quite high, as can be seen in Figure 3, which shows a SEM-image (BSE) of the microstructure in longitudinal direction together with the corresponding distribution of the alloying element Fe according to EDS analysis. The enrichment of Fe in grains alongside of α_p -grains clearly indicates the presence of β -phase in the alloy. Figure 2, right, shows the diffraction pattern of the alloy (smoothed) after a recrystallization treatment at 800°C for 1 h with subsequent air cooling. The corresponding microstructure of the sample is almost identical to the microstructure shown in this figure. As can be seen, only peaks of the α - and β -phase are present. One peak, however, could not be attributed to either α - or β -phase or to Ti_5Si_3 , TiC, or FeTi. The latter might form according to Thermo-Calc[®] simulations.

Figure 2: Left: Globular microstructure (DIC-contrast) of Ti 0.44O 0.5Fe 0.08C 0.4Si 0.1Au (produced in larger quantities) in longitudinal direction after recrystallization (800°C/2h/AC); Right: Diffraction pattern (smoothed) of the same alloy after recrystallization (800°C/1h/AC)

Figure 3: Left: SEM-image (BSE) of Ti 0.44O 0.5Fe 0.08C 0.4Si 0.1Au in longitudinal direction after recrystallization treatment (800°C/2h/AC); Right: Corresponding distribution of Fe according to EDS analysis

Mechanical properties

Table 2 summarizes the mechanical properties of the studied alloys. Additionally, properties of Ti 0.4O 0.08C 0.5Fe (CP-Ti Grade 4⁺), CP-Ti Grade 4, and Ti 6Al 4V ELI, taken from [9], are listed for comparison.

Table 2: Mechanical properties of the studied alloys and comparison with selected titanium alloys

Alloy	Hardness [HV10]	YTS [MPa]	UTS [MPa]	A [%]
Ti 0.42O 0.08C 0.5Fe 0.4Si	311 ¹⁾	971 ¹⁾	983 ¹⁾	16 ¹⁾
Ti 0.44O 0.08C 0.5Fe 0.4Si	313 ¹⁾	987 ¹⁾	993 ¹⁾	15 ¹⁾
Ti 0.40O 0.08C 0.5Fe 2.0Mo	309 ¹⁾	979 ¹⁾	991 ¹⁾	16 ¹⁾
Ti 0.44O 0.08C 0.5Fe 2.0Mo	315 ¹⁾	1006 ¹⁾	1016 ¹⁾	17 ^{1,2)}
Ti 0.40O 0.08C 0.5Fe 2.0Nb	300 ¹⁾	900 ¹⁾	903 ¹⁾	18 ¹⁾
Ti 0.44O 0.08C 0.5Fe 2.0Nb	306 ¹⁾	929 ¹⁾	932 ¹⁾	18 ¹⁾
Ti 0.40O 0.08C 0.5Fe 0.3Si 0.1Au	274 ³⁾	778 ³⁾	846 ³⁾	22 ³⁾
Ti 0.44O 0.08C 0.5Fe 0.4Si 0.1Au	334 ⁴⁾	Not yet investigated		
Ti 0.4O 0.08C 0.5Fe	275 ⁵⁾	690 ⁵⁾	730 ⁵⁾	20 ⁵⁾
CP-Ti Grade 4	220 ⁵⁾	530 ⁵⁾	620 ⁵⁾	19 ⁵⁾
		483 ⁶⁾	550 ⁶⁾	15 ⁶⁾
Ti 6Al 4V ELI	310 ⁵⁾	895 ⁵⁾	930 ⁵⁾	16 ⁵⁾
		795 ⁷⁾	860 ⁷⁾	10 ⁷⁾

¹⁾ Laboratory-size specimens, rotary swaged and recrystallized

²⁾ Minimum ductility, since one specimen failed outside of the tolerated section according to DIN EN ISO 6892-1

³⁾ Material produced in larger quantities, rotary swaged and recrystallized

⁴⁾ Material produced in larger quantities, rolled and recrystallized

⁵⁾ Laboratory-size specimens, rotary swaged and recrystallized; taken from [9]

⁶⁾ Minimum requirements according to ASTM F67

⁷⁾ Minimum requirements according to ASTM F136

In terms of the alloys which have been produced in laboratory conditions, it can be seen that all of them exhibit a higher YTS and UTS than Ti 0.4O 0.08C 0.5Fe and CP-Ti Grade 4 (both alloys produced in laboratory conditions) in combination with a ductility of more than 10% (minimum ductility of Ti 6Al 4V ELI according to ASTM F136). Moreover, they all meet the requirements of Ti 6Al 4V ELI according to ASTM F136. However, in terms of UTS and ductility, not all alloys actually show better mechanical properties than Ti 6Al 4V ELI which has been produced in laboratory conditions. Ti 0.44O 0.08C

0.5Fe 2.0Mo exhibits the highest YTS and UTS of 1006 MPa and 1016 MPa, respectively. In contrast to that, both Nb containing alloys have the lowest static strengths.

These results confirm the expectations, since Mo is a stronger β -stabilizer than Nb [1], whereby the Mo-containing alloys exhibit a higher amount of β -phase, which leads to more phase boundaries, to a better recrystallization and, as a consequence, to better mechanical properties. Si decreases β -transus only slightly [11], but the difference in atomic radius compared to Ti is high, so that Si is a potent solution strengthener. O also significantly distorts the lattice [1], so that even small increases in O-content from 0.40/0.42% to 0.44% lead to a significant increase in YTS and UTS.

Assessment of the fracture surface of the tensile specimens of the alloys which have been produced in laboratory conditions (see Figure 4, which shows exemplarily the fracture surface of Ti 0.42O 0.08C 0.5Fe 0.4Si) revealed mostly dimples and therefore a microscopic ductile fracture [12]. However, local cleavage fractures are present, see Figure 4, right.

Figure 4: Left: Dimples on the fracture surface of Ti 0.42O 0.08C 0.5Fe 0.4Si; Right: Local cleavage fractures of the same alloy

Nevertheless, despite the good mechanical properties of the laboratory-size specimens, it has to be noted that all of them exhibit a high strength ratio. This might be due to the incomplete recrystallization of the specimens as a result of the limited degree of deformation and the potential recovery of the microstructure during rotary swaging, which – as already mentioned – results in a mainly lamellar microstructure.

Ti 0.40O 0.08C 0.5Fe 0.3Si 0.1Au, which has been produced in larger quantities, exhibits a YTS and UTS of 778 MPa and 846 MPa, respectively, in combination with a ductility of 22% in rotary swaged and recrystallized state. Therefore, it does not meet the requirements of Ti 6Al 4V ELI according to ASTM F136. Nevertheless, the mechanical properties are much better compared to CP-Ti Grade 4 and Ti 0.4O 0.08C 0.5Fe (both produced in laboratory-conditions). Moreover, the alloy exhibits an endurance limit of 555 MPa, which is 71% of the measured yield strength.

Ti 0.44O 0.08C 0.5Fe 0.4Si 0.1Au, also produced in larger quantities, shows a hardness of 334 HV10 (rolled and recrystallized) and, therefore, the highest hardness of all mentioned alloys. Tensile tests of this alloy are in preparation at present.

4. Conclusion

In the present study, several alloys on the basis of CP-Ti Grade 4⁺ (Ti 0.4O 0.5Fe 0.08C) for implant and osteosynthesis applications have been studied, which contain O, C, Fe, Au, Si, Nb or Mo as alloying elements. Tensile tests show that all alloys which have been produced in laboratory conditions exhibit a higher YTS, UTS, and elongation at fracture than the minimum requirements of Ti 6Al 4V ELI according to ASTM F136. Although this is not the case for Ti 0.40O 0.08C 0.5Fe 0.3Si 0.1Au (produced in larger scales), the alloy exhibits a much higher YTS and UTS than CP-Ti Grade 4 (produced in laboratory conditions) in combination with an endurance limit of 555 MPa (71% of the measured YTS). As a conclusion, some of the studied alloys might be a promising replacement for Ti 6Al 4V ELI in osteosynthesis and implant applications, since they combine good mechanical properties and a better corrosion resistance with a supposed higher biocompatibility due to the exclusion of Al and V.

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