JOURNAL OF OPTOELECTRONİCS AND ADVANCED MATERİALS Vol. 9, No. 11, November 2007, p. 3389 - 3395

Examination of the properties of Ti-6Al-4V based plates after oral and maxillofacial applications

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The objectives of this study were to investigate corrosion potential and alterations of mechanical features of Ti6Al4V plates after the short-term clinical use. The specimens were examined by imaging microscope, SEM and EDX, stereomicroscope, mechanical and chemical analysis methods. The results of the image analysis showed the presence of topographic alterations on the surfaces. Stereomicroscope examination demonstrated surface damages as surface cracks which occured during handling and application of the material. SEM and EDX results revealed that Ti-6Al-4V plates undergo local erosion due to biological interactions. A noticible decrease in microhardness, tensile strength, fatigue limit and failure values of removed plates was observed. Additionally, serum samples were chemically analysed and determined the concentrations of Ti, Al and V. In conclusion, the experimental results indicated that Ti-6Al-4V based plates have unsufficient corrosion resistance even after short-term clinical usage and they strongly emphasize that removed plates undergo corrosion and their mechanical properties weaken during their clinical function.

(Received March 23, 2007; accepted November 1, 2007)

Keywords: Ti6Al4V plates, Surface structure, Mechanical and chemical analysis, Corrosion

1. Introduction

The interactions between tissue and implant are highly important for its biocompatibility and function. Changes on the surface and structure of the material occur due to oxidation, corrosion, toxicity, and inflammation. These changes reduce the long-term clinical use of the material [1]. Implant material should have optimum combination of mechanical, physical and biological properties. Hence, titanium and its alloys are widely used in biomedical applications [2-5]**.** Ti-6Al-4V has lower elasticity module but good corrosion resistance and biocompatibility than stainless steel and cobalt alloys [6]. However, recent researches indicate that vanadium causes cytotoxic effects and negative tissue reactions and aluminium causes neurological disorders [7]**.**

Titanium alloys do not have high hardness values (24-36 HRC), so they show low wear resistance [8]. The fatigue resistance values of biomedical titanium alloys at 10^7 cycle are between 265-816 MPa, that it has a better fatigue characteristics than other materials [6].

As titanium alloys have the high affinity to oxygene, an oxide film layer rapidly occurs on the surface. Ti gains chemically resistance against corrosion with film layer [9,10]. Implant materials are in contact with both corrosive ions and body fluids like aminoacids and proteins, which accelerate the corrosion. As a result of this interaction, corrosion occurs and metalic ions are released into the body fluids, which may cause allergic and toxic effects [11]. The corrosion resistance is increased by presense of vanadium and chromium [12].

Ti-6Al-4V (Grade 5) is the most popular biomaterial and it consists 5.5–6.75 % Al and 3.5–4.5 % V [13]**.** This alloy has an $\alpha+\beta$ alloy structure and is used in the biomedical applications as a result of its high mechanical features and good corrosion resistance [14].

Immobilization of the fracture segments is essential for fracture treatment [15]. Stable osteosynthesis is a widely used treatment method for mandibular fractures. Titanium and its alloys are mostly preferred as plates and screws. Fractured segments are respositioned and fixed with these materials. [16].

Plate diameters and forms change according to the morphology of the treatment area [17]. Altough it is thought that titanium and its alloys have generally good biocompatibility properties, the researches on interaction between cells and titanium surface were shown controversary results. Disegi indicated that vanadium element has a toxic effect in the body [18]. A tissue cover formation has been reported in a study about titanium plates used for maxillofacial surgery on monkeys during removal of plates [19]. A previous study is demonstrated that infection is a very imporant reason for removal of the osteosynthesis materials [20]. Metallic chips were formed during adaptation and fixation of plates with screws by the abrasion and these metallic chips were be infiltrated into the tissues [21].

Mini-, micro- and compression titanium based plates are widely used in oral and maxillofacial surgery. They are produced for long-term use in the organism, but they are clinically used for 6 months and 1 year in oral and maxillofacial surgery. However, their chemical and mechanical properties were not sufficiently examined previously for short-term applications. Our purpose was to investigate their corrosion potential and alterations of mechanical features. Recent researches for long-term period showed that especially Ti-6Al-4V alloys were released titanium, aluminium and vanadium species to biological medium [9,19-21]. These researches are also begun for short-term applications [22].

2. Experimental methods

The study was included a total of 7 Ti-6Al-4V based miniplates as shown in Fig. 1A. The plates had been implanted for fixation after mandibular fractures in Marmara University, Faculty of Dentistry, Division of Oral and Maxillofacial Surgery (Fig. 1B). After 24 weeks, titanium plates were retrieved from 4 patients.

Insertion of the plates was performed by 2 experienced oral surgeons. Hole plates with screws placed on each side of the fracture line were examined. Adaptation to the bone surface by bending of the plates had been performed in all cases. Titanium plates had been implanted for 24 weeks. All the plates were removed without preceding clinical complications. After careful removal all compenents of devices were immediately rinsed in tap water, carefully cleaned with a soft brush in an organic solvent, followed by ultrasonic treatment in ethanol for 5 minutes. The specimens were stored dry until examination.

To compare their physical properties and corrosion potential, original samples were tested as control groups. The images of control and clinically used plates are shown in Fig. 1A. The control and used samples are examined about macrostructure, microsructure, surface, mechanical and corrosion properties and the results are compared to each other.

Superior (soft tissue) and inferior (bone) surfaces of control and removed plates were examined with imaging microscope (Leica DMLM) before metallographic procedures. Therefore, the surface properties of original and clinically used plates were compared.

The samples exposed cutting, moulding, grinding, polishing and etching treatments were examined microstructures by SEM (JEOL JSM-5410LV Scanning Electron Microscope). The composition of clinically used plates were examined with energy dispersive X-ray analysis (EDX). This analysis revealed the ratio of elements within the plates, and also presence of any element transfer from the biologic environment into the structure.

The surfaces of specimens were examined with stereomicroscope three dimensionally. Screw holes, scracthes and cracks on the materials were displayed (Leica MZ7.5 model Stereomicroscope, Leica DFC280 Digital Camera).

The hardness values of the samples were measured with microhardness device (Zwick 3212001) after grinding process. Applied load and loading time is 200 g and 20 s. The microhardness unit was transformed into Vickers hardness value and than also Brinell hardness. Tensile strength values of the plates were calculated according to equation 1 and the measured hardness values. These values were compared with given in the literature tensile strength values in the literature [6,23,24]. The results showed that the tensile strength values of Ti-6Al-4V plates could be calculated using measured hardness values and equation 1. Based on this result, tensile strength of Ti-6Al-4V plates were calculated using measured hardness values and equation 1[25,26,27].

$$\sigma_{TS} = 3.5 \times (HB) \tag{1}$$

σ_{TS}: Tensile strength, HB: Hardness Brinell.

Most of the materials work under cycling loads and vibrations during their function. These working conditions cause cracks on the surfaces and fractures after a specific cycle number. This event, which is called "fatigue", and it is the cause of approximately 90% of mechanical damages in the metals. Fatigue cracking generally starts in a notch, scratch, microflow, corrosion area and geometrical structures (like screw holes). Fatigue values were calculated according to equation 2 and the tensile strength values. These calculated values were compared with fatigue values in the literature [6,23,24]. The results showed that the fatigue values of Ti-6Al-4V plates could be calculated using measured tensile strength values and equation 2. Based on this result, fatigue of Ti-6Al-4V plates were calculated using measured tensile strength and equation 2 [27].

$$\text{Fatigue Limit} = 0.5 \times (\sigma_{TS}) \tag{2}$$

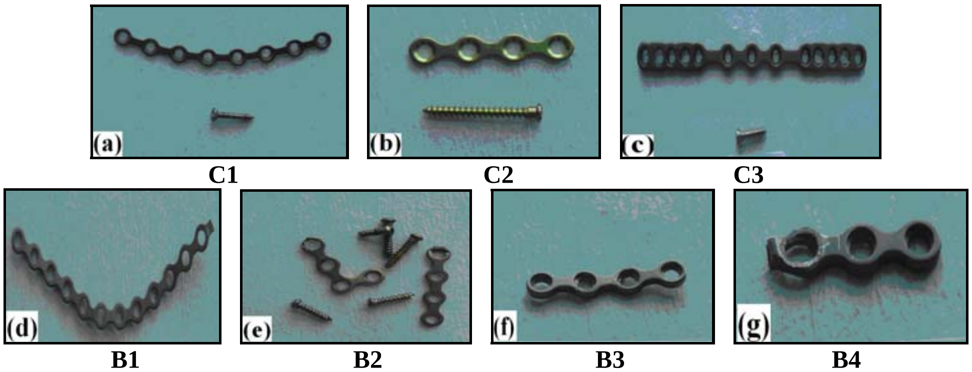
Maximum strength of Ti-6Al-4V plates is obtained by failure test (Universal test machine). During failure test, applied loads on the samples form both a compression strength and tensile strength on the different parts of the sample. These strengths cause bending of the sample. During the bending test, the load used is 50 Kg. Failure strength is calculated using by equation 3.

$$\sigma_{Fracture} = 1{,}5\ (F \times L) / (b \times h^2)\ \ (\text{kg/mm}^2) \tag{3}$$

F:load (kg), L: distance (mm), b: width (mm),
h: heigth (mm)

10 ml blood samples were collected from three patients (B1, B2, B3 and B4) 6 months after implantation. Serum samples were analized with graphite furnace atomic absorption spectrophotometer (GF-AAS).

(A)



(B)

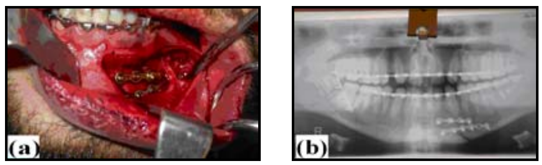


Fig. 1. (A) Images of control plates and plates removed from the body: (a) microplate-C1, (b) miniplate-C2, (c) miniplate-C3, (d) microplate-B1, (e) microplate-B2, (f) miniplate-B3, (g) miniplate-B6. (B) Osteosynthesis treatment (a) intraoral and (b) radiographic appearance of miniplates.

3. Results and discussion

Superior (soft tissue) and inferior (bone) surfaces of control and removed plates were examined with imaging microscope before metallographic procedures (Fig. 2).

When C1 (Fig. 2-C1) and B1 (Fig. 2-B1) microplates were compared, microtopographic alterations were observed in superior surface of B1 microplate (Fig. 2-B1/a). Effects of compression forces on microplates used in maxillary fractures were more prominent. Porous structure of original surface was lost during clinical use. Therefore biochemical products were covered on the plate surfaces (Fig. 2-B1/b). When C2 (Fig. 2-C2) and B3 (Fig. 2-B3) miniplates were compared, some orientations due to tensile strength on the surface were observed (Fig. 2-B3/a). However, no orientation was observed through the superior surface of the C2 plate (Fig. 2-C2/a) . It is thought that tension and compression forces and biological interactions can modify the surface of the plate. It is thought that these structures are formed as a result of biological interactions between tissue and metal. Original surface structure (C2 plate) was changed completely and new biolayers occured on the surface of B3 plate. It is observed that superior surface of B3 used in mandibular fractures (Fig. 2-B3/a) was completely covered with a biochemical layer. Biochemical interactions were observed locally as white zones on inferior surface (Fig. 2-B3/b). In the left side and middle of inferior surface of B3 sample (Fig. 2-B3/b), different orientations were seen. There was almost no difference between inferior and superior surfaces of B4 sample (Fig. 2-B4/a and Fig. 2-B4/b).

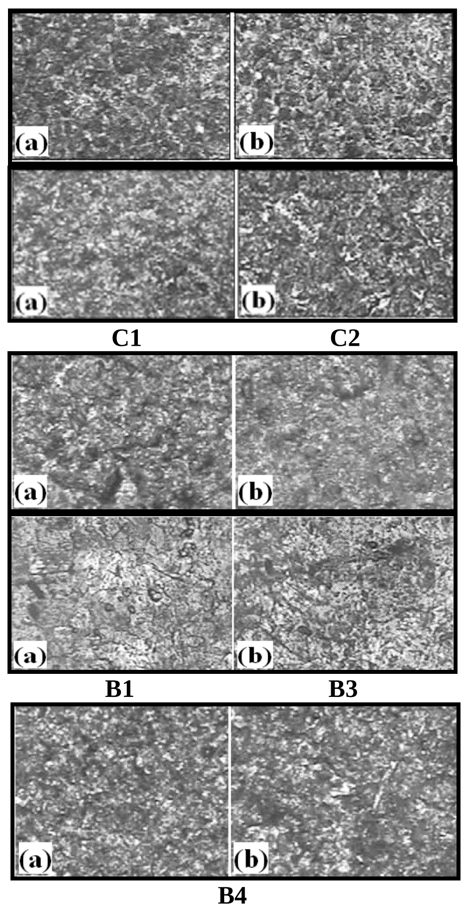


Fig. 2. Images of superior (a) and inferior (b) surfaces of control plates (C) and plates removed from the body (B), (magnification x200).

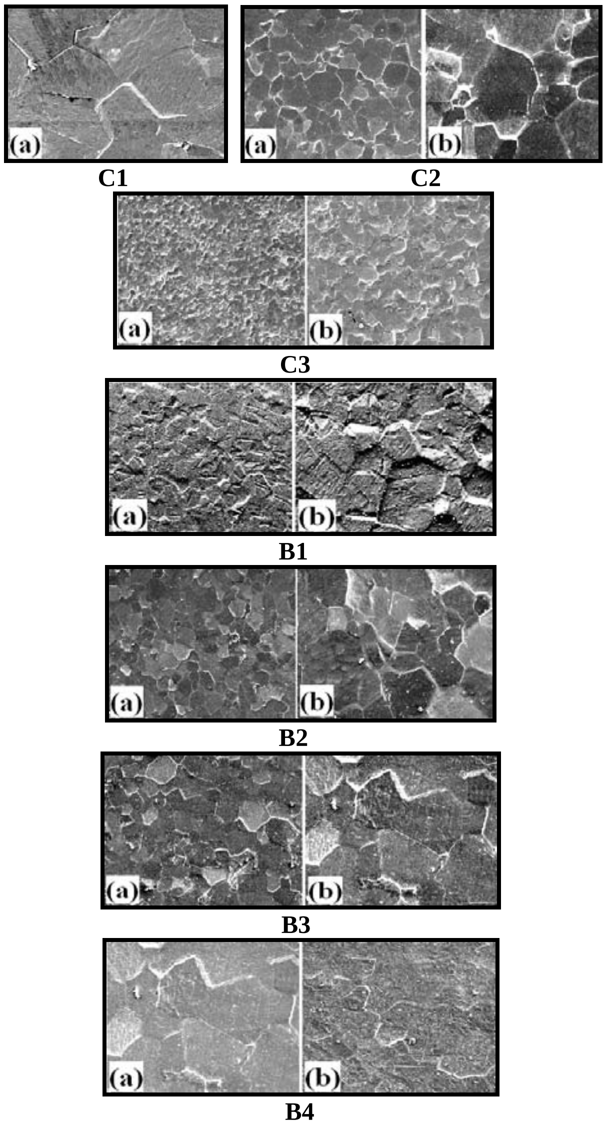
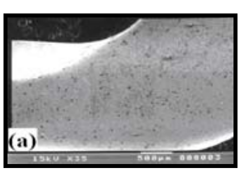
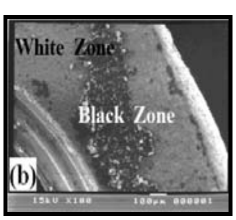


Fig. 3. SEM images of control plates and plates removed from the body: (a) magnification x200 and (b) magnification x500.



Element	Concentration (% wt.)
Ti	90.520
Al	5.875
V	3.605



White zone		Black zone	
Element	Concentration (% wt.)	Element	Concentration (% wt.)
C	35.06	Ti	95.798
O	7.67	Al	1.458
Si	57.27	V	2.744

Fig. 4. SEM images and EDX analysis of (a) C1 and (b) B1 plates.

Microstructures of removed mini- and microplates were investigated with SEM. SEM images of the control and removed samples were given in Fig. 3 and Fig. 4, respectively. SEM examinations were shown that original plates (C1, C2 and C3) have (α+β) structure (Fig. 3). Grey structures in these images are α phase and also darker zones are β phase. High β ratio is desired to provide high mechanical and corrosion resistance in titanium plates [25]. It was observed that particle size of C3 sample is finer than particle size of C1 and C2 (Fig. 3-C1/a, C2/a and C3/a). Small particle size increases toughness value of materials. C1 plate was used for mandibular fractures and it should be effected by compression forces. Thus, higher toughness values are required for these plates which will be used mandibular fracture treatment. B1 and B2 microplates present lower hardness value (140 and 148 HV) when compared with C1 microplate (160 HV). SEM images of B1 and B2 plates (Fig. 3-B1 and Fig. 3-B2) were shown that their microstructure and particle size properties are at the same level with C1. But SEM images of B3 and B4 plates (Fig. 3-B3 and Fig. 3-B4) were shown that microstructure and particle size properties of B3 and B4 microplates are at the same level with C2. These plates have similar strenght properties because they are used in maxilla (B1) and mandible (B2). As miniplates are used in fracture treatment, their average particle size must be higher than microplates. Mechanical properties of B3 and B4 plates decreased when compared with C2 and C3. It can be stated that smaller grain size provides higher mechanical properties (hardness value, tensile, compression and failure strengths).

EDX analysis of C1 microplate (control plate) showed standard alloy composition of Ti6Al4V (Fig. 4-a)). It was indicated that there are 90.52 % Ti, 5.875 % Al and 3.605 % V elements in the structure. Analysis values obtained from two different areas of B2 microplate are given in Fig. 4-b. Carbon, oxygen and silicon elements are also determined besides Ti, Al and V elements. Presence of carbon and oxygen elements shows that there is an interaction between plate surfaces and surrounding tissues. Ti-6Al-4V plates are corroded locally during clinic use according to the results of EDX analysis. Decreased Al and V values on the tested plate surface also support this outcome.

Three dimensional examinations of titanium plates were performed with stereomicroscope (Fig. 5). Stereomicroscopic examination revealed presence of a long crack on the narrow area of B1 plate (Fig. 5-B1/a-k). The image of this crack indicates that there are very significant deformations (Fig. 5-B1/b). m area on the B3 plate may be formed as a result of plastic deformation (Fig. 5-B3/a-m). Fig. 5-B3/b was revealed a significant damage on the surface. Stereomicroscope image of C1 (control) was not exhibited surface defects (Fig. 5-C1). When C1 control sample was compared with removed plates (B1 and B3), we observed important mechanical and chemical changes on their surfaces after 6 months of clinical use.

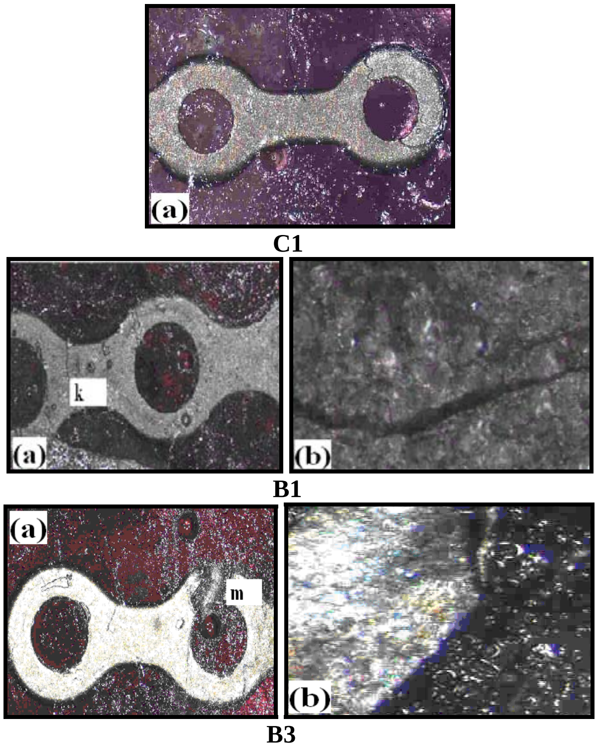


Fig. 5. Stereomicroscope images of C1, B1 and B3 plates: (a)magnification x6.3, (b) magnification x25.

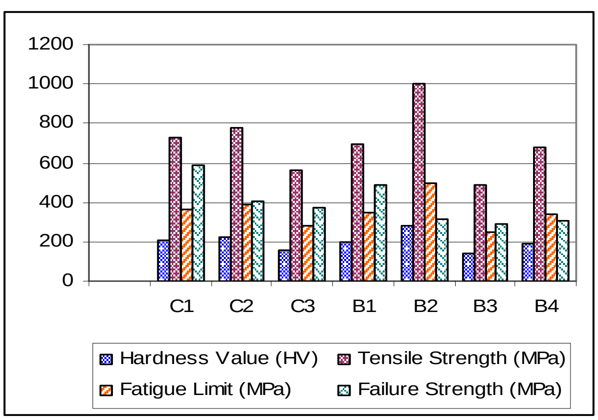


Fig. 6. Hardness, tensile, fatigue and failure strength values of removed Ti-6Al-4V plates from human body.

The results of applied mechanical tests to plates are given in Fig. 6. Hardness value of B1 microplate had 20 HV lower value than C1. Hardness of B2 microplate decreased 12 HV according to C1. Hardness of B3 microplate decreased 16 HV according to C1 and 28 HV according to the C2. When B4 micro plate had 23 and 35 HV lower values when compared with C2 and C3 plates, respectively. B3 micro plate has the minimum hardness value. These changes can be explained as the results of handling defects, localization and shape of plates and metal losses.

Measured hardness values put into the equation (1) and tensile strength values are calculated. Calculated tensile strength values put into equation (2) and fatigue limit values are calculated. It is indicated that the calculated tensile strength and fatigue limit values by using the hardness values of Ti-6Al-4V alloy given in litreature are similar to the values in the literature. So fatigue limit showed the maximum fatigue load, the material should be worked under this value. Measured failure strength (σ_{FT}) values in used plates were decreased according to original plates. If the plates fixed in mandible area were exposured to higher loads than given values, they will bend.

10 ml blood samples were collected from 4 patients (B1, B2, B3 and B4) 6 months after implantation. Serum samples were analized with graphite furnace atomic absorption spectrophotometer (GF-AAS). The quantities of metal relesed from implants into human body in clinical literature (in vivo) were compared with metal releases observed in this study. The average and range serum Ti, Al and V levels in this study were found 10.7 (9.5-11.9), 3.82 (3.26-4.51) and 20.22 (16.29-25.56) ng/ml, respectively (Fig. 7). A serum aluminium level of 10 ng/ml or less is internationally accepted as safe [28], the avarage serum Al level in this study was 3.82 ng/ml, which is slightly below the limit**.** Jacops et al reported Ti, Al and V concentrations (mean and range, or mean±SD) in serum from patients without implants as follows: Ti: 4.10 (2.11- 7.92); Al: 2.15±0.51 and V: below 0.81 ng/ml, respectively [29]. Preoperative mean Ti and Al concentrations (range) in serum were determined 1.4 (1.10-3.60) and 1.32 ±0.23 ng/ml [30]. The avarage serum Ti, Al and V levels in this study were 10.7, 3.82 and 20.22 ng/ml, which is slightly above the preoperative values in the literature**.** However, Ti, Al and V concentrations in serum patients with loose total hip replacement (21 patients) made of Ti-6Al-4V alloy at a mean duration of 44 months were detected 8.08 (<2.11-17.2), 2.16±0.26 and 1.30 (< 0.81-1.60) ng/ml [29]**.** Ti concentration (mean: 135.57, range: 24.12-716.94 ng/ml) in serum of 20 patients was found approximately 50 times grater in patients with failed Ti-6Al-4V alloy total knee replacements of 8 patients and mean duration of implantation of 57 months [30]. The quantities of released Ti, Al and V from alloy for short-term application (Fig.7) were also exceed literature values when they compared with values after the operation [29,30]. Whereas, these values should be lower than those of long-term applications (44 and 57 months). Vanadium releasing is approximately two times more than titanium value and five times more than aluminium value.

In this study, serum samples from patients were not taken before the operation. However, baseline values of patients have to be known to compare with each others. For this reason, patient serums should also be necessarily analyzed before the operation. For further studies, preoperative serum levels will be determined and the larger study groups will worked out.

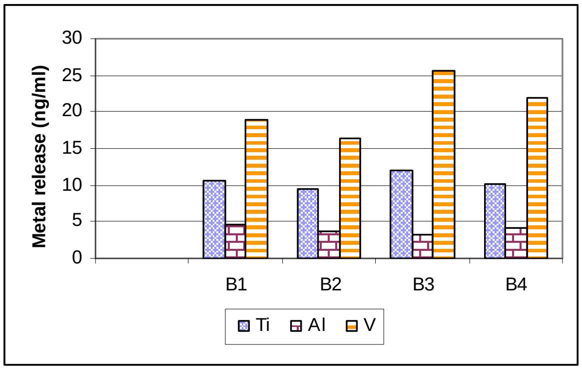


Fig. 7. Serum analysis of patiens whose implants are taken out.

4. Conclusions

We observed that mechanical values of plates decreased and metal release from the plates was realized in the serum after clinical use of titanium plates. During fixation and extraction of the plates, scratches occured on the plates were enhanced the metal release. Additionally, manufacturing processes and clinical applications were made weak the physical properties of the material. Metals were released into surrounding tissue from oral and maxillofacial implants by various mechanisms, including corrosion, wear and mechanically accelerated electrochemical processes such as stress corrosion, corrosion fatigue and fretting corrosion. This metal release has been associated with clinical implant failure, osteolysis, cutaneous allergic reactions, and remote site accumulation**.** Hence, these materials should be removed from the body when their function is completed. Although high surgical operation and materials costs, they should be removed from the body and shouldn't be reused for another patient even for short-term applications as 6 months. New implant alloys should be designed without toxic elements to eliminate the possible side effects into the body. Zr, Nb and Ta additions to Ti were shown excellent compatibility in both hard and soft tissues, and inhibited metal release [31].

Acknowledgements

The authors would like to acknowledge Karacan Group Co. for their material support. We also wish to express our thanks to the Departments of Bioengeering and Metallurgical and Material Engineering, Chemistry-Metallurgy Faculty, Yıldız Technical University for supplying the scientific research for this study. We thank Dr. Seval Bayülgen for carrying out the chemical analysis.

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