Investigation on microstructure, surface and corrosion characteristics of heat treated AISI 420 martensitic stainless steel laser welds in simulated body fluid (SBF)

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Aim of the present study was to investigate metallurgical properties of pre- and post-weld heat treated and non-heat treated AISI 420 martensitic stainless steel joined using CO_2 laser welding method. In addition, heat treated laser welded and base metal samples were immersed in Simulated Body Fluid (SBF) for 1, 3, 7, 14, 21 and 28 days, and apatite formations on base metal and on welding seam surface were studied. Corrosion properties on all samples immersed in SBF were determined based on weight loss method. Due to heat treatment process, corrosion sensitivity occurred by producing carbides, such as $Cr_{23}C_6$, $M_{23}C_6$, and decreasing local chromium content in the weld zone. In addition, weld heat input affected corrosion resistance.

Keywords: Laser welding; Martensitic stainless steel, Heat treatment; Microstructure; Surface; Corrosion.

1. INTRODUCTION

Martensitic stainless steels rely on Fe-Cr-C ternary phase equilibrium diagram system. These steels can show transitions from martensitic phase to austenite phase through many thermomechanical processes via allotropic transition. Except for very slow cooling conditions inside a furnace, these phase changes could be experienced [1]. Martensitic stainless steels are generally used as quenched and tempered or annealed. These steels resemble ferritic stainless steels in terms of chemical composition, but they contain higher carbon and less chromium, and thus they could be hardened through heat treatments [2]. Martensitic stainless steel exhibits tough and brittle structured martensitic formation due to its nature even when it is cooled very slowly. Martensitic phase triggers formation of

microcracks in weld zone and causes welding seam to have tendency of fracture. This is the main reason why martensitic stainless steels have poor weldability [3-5]. However, these type of steels can be joined through heat treatments before and after welding, and desired strength properties are achieved [5]. Because of their superior mechanical properties and resistance to corrosion, martensitic stainless steels are used in manufacturing of water and vapor valves, turbines, pumps, shafts, ball bearings, cutting, and surgical tools [1, 6-9].

AISI 420 martensitic stainless steels can be graded in ISO 7153-1 (Surgical instruments-Metallic Materials-Part 1-Stainless Steel) and are defined as a material used in production of surgical tools but not used directly as implant in human body (non-implant) [10]. However, AISI 420 martensitic stainless steel is used in manufacturing of orthopedics, such as artificial knee joint components, tool, and jigs due to their superior hardness, strength and resistance to corrosion properties [11,12].

Certain tests are necessary to determine corrosion properties of stainless steels to be used in human body as implants [13]. Determination of corrosion resistance of stainless steels in laboratory conditions using Simulated Body Fluid by an in vitro test is one of these methods [13, 14]. This study becomes important since there is no study in the literature investigating the behavior of corrosion as a result of the immersion of laser welded AISI 420 martensitic stainless steel in Simulated Body Fluid (SBF). In the present study, microstructural characterization is carried out for both pre- and post-weld heat treated and non-heat treated AISI 420 martensitic stainless steel joined using CO₂ laser welding process. In addition, apatite morphology formed at the surface of heat treated laser weldments and base metal samples immersed in SBF for 28 days were examined, and corrosion resistance by samples immersed in SBF was determined using weight loss method. It is also important to note that because cold crack occurs in welding seam of non-heat treated samples, they are not immersed in SBF. Thereby only heat treated samples were immersed in SBF.

2. EXPERIMENTAL STUDIES

2.1. Material, heat treatment and welding procedure

AISI 420 martensitic stainless steel, used in many industries and especially for manufacturing of surgical tool and instruments, were used in the present study. Table 1 shows the chemical composition of AISI 420 stainless steel.

Table 1. The chemical composition of AISI 420 stainless steel (wt%).

С%	Si	Mn	Р	S	Cr	Mo	Ni	Al	Со
0.351	0.562	0.548	0.024	0.0090	13.71	0.084	< 0.300	< 0.002	0.015
Cu	Nb	Ti	V	W	Pb	Sn	Zn	Ν	Fe

AISI 420 steel plates were joined at different two welding speeds at flat position without any additional metal using a TRUMPF LASERCELL 1005 type CO₂ laser welding machine of 4kW power with parameters specified in Table 2. Prior to welding, samples were preheated at 300 $^{\circ}$ C for 60 minutes, and after welding they were tempered at 660 $^{\circ}$ C for 75 minutes, and then cooled to room temperature in a furnace. The non-heat treated sample that we observe cold crack was joined with 4000W-70cm/min (0.342kJ/mm heat input) under the parameters of shielding gas, gas flow rate, and focal length as shown in Table 2, by using the same laser welding machine mentioned above. It is also important to note that cracking in weld metal occurred in non-heat treated samples after laser welding trials under different welding parameters.

 CO_2 laser welding is superior to traditional welding methods, and it is used in the present study due to low heat input, high condensation energy, fast welding process, narrow weld zone, deep penetration, suitability to automation, high mechanical strength, low distortion, and welding without use of additional wire [15-23].

Sample code	Laser power (Watt)	Travel speed (cm/min)	Shielding gas	Gas flow rate (lt/min)	Focal length (mm)	Heat input (kJ/mm)
B1	3500	180	50% Ar + 50% He	10	200	0.116
B2	4000	180	50 Ar% + 50% He	10	200	0.133

Table 2. The laser welding parameters of heat treated samples.

2.2. Preparation of experimental samples and characterization studies

In order to characterize in detail the microstructural changes in heat treated and non-heat traeted experimental samples, three different etching procedures were applied in a row: a) etching with 10g oxalic acid + 100 ml distilled H₂O etched electrolytically, b) etching with potassium hydroxide + distilled H₂O, and c) etching with Villela's solution (1g picric acid + hydrochloric acid + 100ml ethanol). Microstructural examinations were carried out using 5x-100x magnified OLYMPOS brand optical microscope and JEOL JSM 6060 LV brand scanning electron microscope (SEM) with EDS equipment.

For corrosion and surface characterization studies, laser welded and base metal of heat treated samples were cut 20 x 5 x 3 mm³ sizes and were polished by 200-2000 grit sand-paper. After polishing process, all samples were washed in an ultrasonic bath first with acetone and then with deionized water for 30 minutes. After washing, samples were dried in an over at 50 °C, weighed in an analytical balance and then immersed in SBF solution. After immersing in SBF solution for 1, 3, 7, 14, 21 and 28 days, samples were taken out, rinsed with deionized water, left to drying at room temperature, weighed again in analytical balance and their weight changes were calculated. After, apatite structure

accumulated on the surface of laser welded and base metal was studied using SEM and EDS. After studying the apatite structure accumulated on the surface, all samples were immersed in acidic solution prepared according to ASTM G1 [24], and corrosion products accumulated on their surface were removed. Then, final weight changes of laser welded samples were determined and their microstructural characterizations were carried out via SEM, EDS.

2.3. Weight gain, weight loss and corrosion experiment

For this study, Simulated Body Fluid solution developed by Kokubo was used [25]. Each tool used for the preparation of solution was pre-sterilized. Temperature of the environment was fixed at 36-37 °C during all phases of solution preparation. SBF chemicals were Merck brand, and they were added to the solution in a fixed row, and pH was adjusted to 7.4 which is a pH level close to human blood plasma.

After preparation of SBF solution, laser welded and base metal of heat treated samples were immersed in SBF solution at 36.5 °C and immersed for 1, 3, 7, 14, 21 and 28 days. Throughout the experiment, SBF was replaced in every other day and thus original ion concentration was maintained. For each immersion period, all samples removed from SBF solution was washed by deionized water, allowed to dry at room temperature, and weight changes were determined by weighing in an analytical balance and calculating the difference. In order to eliminate corrosion products accumulated on the surface of all samples, 100 ml nitric acid (HNO₃), one of the chemical cleaning solutions given in ASTM G1, was prepared. All samples were kept in an ultrasonic bath at 60 °C for 20 minutes, then removed, washed by deionized water and dried in an incubator at 50 °C. Final weights of all samples were determined by weighing in an analytical balance. Corrosion rates of all samples based on weight loss were calculated using the following formula:

Corrosion rate = $(K \times W) / (A \times T \times D)$

K: Constant, W: Loss of mass (g), A: Surface area (cm²), T: Duration of the experiment (hours), D: Density of the material (g/cm^3)

3. RESULTS AND DISCUSSION

3.1. Microstructural examinations

Optical microscopic images of non-heat treated laser welded AISI 420 martensitic stainless steel (Figure 1) revealed that a certain amount of grain growth due to fast cooling depending upon heat input were realized along with a narrow HAZ formation. In weld metal, on the other hand, a predominantly martensitic microstructure was obtained due to lack of necessary time as a result of fast cooling needed for structural transformation. Predominant martensitic nature of weld metal microstructure was the main reason leading to formation of cracks via triggering cold crack propagation (Figure 1). It was understood that weld metal changed its microstructure from cellular grain structure to columnar and equiaxed dendritic grain structure during solidification process of weld metal. Microstructure of weld metal was predominantly of martensitic nature (Figure 1).





Figure 1. The etched non-heat treated of laser welded sample's microstructure images; the non-heat treated sample was oxalic acid etched, (a) base metal, (b) HAZ, (c) the formation of cold cracks in weld metal, (d,e) weld metal, the non-heat treated sample was Villela's reagent etched, (f) HAZ, (g) weld metal, the non-heat treated sample was potassium hydroxide etched, (h) HAZ, (i) weld metal.

Microstructural changes in heat treated samples, on the other hand, showed that grain growth occurred especially in HAZ and carbide collapses developed depending upon heat input transferred to weld zone and upon whether pre- and postweld heat treatment process was applied (Figure 2 and 3).





Figure 2. The heat treated sample B1 was oxalic acid etched, (a) HAZ, (b) weld metal, the heat treated sample was Villela's reagent etched, (c) HAZ, (d) weld metal, the heat treated sample was potassium hydroxide etched, (e) HAZ, (f) weld metal.



Figure 3. SEM images of laser weldment, the heat treated sample was oxalic acid etched, (a) weld metal, (b) HAZ of sample B1, (c) base metal, (d) weld metal of sample B2.

Depending upon tempering heat treatment process at 660 °C for 75 minutes after welding and cooling inside an oven, tempered martensitic structures, slight amount of residual δ -ferrite and very small amounts of carbide collapses were clearly observed in microstructure images of weld metal

(Figure 2 and 3). It is known that δ -ferrite phase has lower resistance to corrosion compared to austenite matrix [26,27]. Based on microstructural examination of heat treated sample, no crack or pore formation was observed in HAZ and weld metal.

In addition, EDS point analysis was performed in base metal, weld metal, and HAZ of B1 and B2 samples. The results are given in Figure 4. Furthermore, weld metal was analyzed via elemental mapping analysis, and results are shown in Figure 5. A comparison of EDS analysis and elemental mapping shown in Figure 4 and Figure 5 along with spectral analysis results of AISI 420 stainless steel (Table 1) suggest that no marked losses of alloy elements occurred due to welding process. However, EDS point analysis results showed that carbide collapses such as $M_{23}C_6$, $Cr_{23}C_6$ that occurred in weld metal and in HAZ resulted in clear decreases in Cr amounts in alloy element of weld metal as a result of tempering heat treatment carried out after welding and during the cooling period of sample inside an oven. Decrease in amount of chromium was somewhat more in B2 sample. In EDS and elemental mapping analyses, less than 12% of chromium was detected, which is the limit for passive film formation, and this amount is expected to cause the formation of local corrosion in weld metal and HAZ.



Figure 4. EDS analysis of B1 and B2 samples, the heat treated sample was oxalic acid etched, (a) EDS analysis, (b) elemental mapping analysis.

3.2. Weight gain

Amount of apatite formed on the surface of all samples after immersing in SBF for different periods was measured using an analytical balance with a 0.0001 g sensitivity. Effect of immersion period in SBF on apatite formation on the surface of samples is shown in Figure 5. Weight gains due to covering of surface of samples with apatite layer after immersing in SBF was calculated using the following formula:

Weight gain = (Weight after immersing in SBF – weight before SBF experiment) / surface area of sample.



Figure 5. Weight gains by base metal and B1 and B2 laser welded of heat treated samples immersed in SBF for 1, 3, 7, 14, 21 and 28 days

Increase in the thickness of hydroxyapatite layer accumulated on the surface of joint of AISI 420 martensitic stainless steel for different two welding parameters depending upon prolonging immersion period in SBF is clearly seen in Figure 5. As the welding heat input increased, thickness of hydroxyapatite layer, consequently the weight gain, tended to increase. It is hypothesized that laser welded samples affected by weld thermal cycle was promoted to accumulate more apatite mineral by the effect of SBF solution. Hydroxyapatite layer accumulated on the surface of base metal was somewhat higher than that of welded joints for all immersion periods. This result could be due to the effect of pre- and postweld heat treatment process applied to laser welded as well as due to weight gain as a result of corrosion which occurred in experimental samples during immersion in SBF. It was reported that nickel free martensitic stainless steel, preferred for the manufacturing of surgical cutting tools, could have apatite development on the surface and potential bioactivity properties during immersion period in SBF fluid up to 28 days.

Although base metal and laser welded samples were immersed in SBF for the same time period, more apatite accumulation was observed on the surface of base metal. Thus, it appears that a better apatite nucleation and growth took place on the surface of base metal. In addition, it could be concluded that less amount of apatite formation was realized on welding seam due to weld thermal cycle or that apatite layer had less bioadhesive strength on welding seam compared to base metal. It could be concluded that bioactivity properties on welding seam of laser welded samples were lower, though slightly, compared to base metal surfaces.

3.3. Surface morphology

Basically, in vitro apatite forming abilities of implant material or biomaterial surfaces are determined by immersing the material into SBF and measuring [28, 29]. Ability of implant materials to develop and to grow apatite on their surfaces is associated with the ability of surface of that material to have bioactive properties. Materials which have apatite formation on their surfaces can also develop apatite on living bone tissue. In addition, bone attachment and bone growth on apatite layer could occur [30]. SEM examinations of welding seam in laser welded samples revealed that surfaces of samples were covered with apatite at the end of 28th day. SEM examinations also showed that apatite formation did not have a homogeneous distribution on surfaces and had a nano-porous apatite morphology due to the effect of weld metal and HAZ width depending upon joining of AISI 420 stainless steel samples with different welding parameters as well as due to their different heat inputs (Figure 6).



Figure 6. SEM image of apatite formation taking place on surface of base metal (7a and 28a) and on welding seam of laser welded B1 (7b and 28b) and B2 (7c and 28c) heat treated samples immersed in SBF for 7 and 28 days.

EDS analysis was carried out on welding seam of laser welded samples and on anywhere on base metal which were immersed in SBF for 28 days (Figure 7).

EDS examinations showed the formation of Ca, P, O and Na elements, main constituents of hydroxyapatite, a structure similar to bone tissue, on the base metal sample and on the surface of welding seam. EDS analysis conducted on hydroxyapatite layer formed on the surface of welding seam of samples immersed in SBF up to 28 days revealed that Ca/P ratio tended to increase as the duration of immersion in SBF increased.



Figure 7. EDS point analysis of apatite form that developed on surface (a) base metal, (b) on welding seam of laser welded B1, (c) B2 heat treated samples immersed in SBF for 28 days.

This finding indicates that prolonged immersion might lead to an increase in hydroxyapatite and it shows that apatite accumulation on the surfaces may accelerate depending upon immersion period. Ca/P ratio on the surface of base metal sample immersed in SBF for 28 days was about 1.02, while it was 1.04 and 1.10 on welding seam of laser welded B1 sample and B2 sample, respectively. The ratios in EDS analyses were smaller in early days of immersion (about 0.80-0.90 Ca/P ratio).

Characterization of apatite structure which developed on welding seam after immersing the sample for 28 days in SBF via EDS revealed that the value of stoichiometric Ca/P value of hydroxyapatite for the ratio of bioactive Ca and P ions (Ca/P), ingredients of apatite structure, was less than 1.67. Also, Ca/P ratios of samples were similar to each other. Stoichiometric Ca/P value of hydroxyapatite is 1.67. However, when Ca/P ratios of apatite layer that accumulated on welding seam of laser welded AISI 420 stainless steel samples and on the surface of base metal samples which were immersed in SBF are lower than 1.67. That can be called as calcium deficient carbonate hydroxyapatite structure with low crystallinity [31, 32]. There are many types of hydroxyapatite and they are classified based on Ca/P ratio [31].

3.4. Weight loss and corrosion resistance

Weight loss results of laser welded and base metal samples immersed in SBF for 1, 3, 7, 14, 21 and 28 days are given in Figure 8. Base metal samples incurred less weight loss compared to samples joined using different two laser welding speeds, which was indeed an expected result (Figure 8).



Figure 8. Weight loss rates of AISI 420 stainless steel Base metal and B1 and B2 heat treated samples immersed in SBF for 1-28 days

Results clearly indicate a weight loss in base metal and laser welded samples depending upon the duration of immersion in SBF (Figure 8). Although AISI 420 stainless steel samples had been joined via laser welding method with low heat input, it was clear that samples were affected by weld thermal cycle, and a sensitivity occurred in weld metal or HAZ compared to base metal, and this sensitivity resulted in weight loss in laser welded samples. It should also be mentioned that the weight losses here were in considerable amounts. The main reason for such a result was relatively limited chemical composition of AISI 420 martensitic stainless steels compared to other stainless steel types. Considering the weight loss of base metal and laser welded samples immersed in SBF for 28 days, weight loss was 0.0025 g in base metal, 0.0029 g in sample B1, and 0.0046 g in sample B2. It appears that in general weight loss in AISI martensitic stainless steel samples during the immersion in SBF was affected by heat input. It was observed that B1 sample joined with lower heat input had less weight loss. Protective oxide layer that formed on the surface of laser welded and base metal supported the stability of samples against weight loss during immersion in SBF. It is important to note that stainless steels produce a passive oxide film on their surfaces with passivation process as a result of their chromium content [Fe,Ni)O(Fe,Cr)₂O₃]. In physiological conditions, chrome oxide layer forming on the surface [13, 33] prevents the transport of metallic ions and electrons, thereby lowering corrosion rate [33].

Corrosion rates of laser welded and base metal samples in SBF calculated based on weight loss were given in Figure 9.



Figure 9. Corrosion rates of base metal, B1and B2 heat treated samples immersed in SBF for 28 days.

Relatively high corrosion rates in laser welded and base metal samples are given in Figure 9. When we consider the corrosion rates of samples from laser welded AISI 420 stainless steel, it could be seen that different two welding parameters used for joining the samples led to different corrosion rates. Different corrosion rates observed in samples could be due to different heat inputs as well as due to carbide collapses observed especially in HAZ. In addition, similar observed corrosion rates in base metal and welded samples could essentially be due to heat treatment process applied to martensitic stainless steel. Insufficient resistance of samples to corrosion could be due to 0.035% carbon content of

AISI 420 martensitic stainless steel experimental samples, and relatively low chromium, nickel, and molybdenum content compared to other stainless steel types.

By covering surface of metallic implant of biocompatible organic hydroxyapatite and by preventing metallic ions to dissolve, the corrosion occurrence delays [34, 35] and resistant to corrosion increases [36]. Increased apatite layer accumulating on the surface of samples as a result of prolonged immersion in SBF is expected to prevent weight loss from samples in SBF environment and release of metallic ions, thereby decreasing corrosion rate. The fact that the surface of all samples immersed in SBF, which is not completely covered with apatite in early days or weeks of the immersion, could lead to variations in corrosion rates of samples in some immersion periods, because bare parts of samples not completely covered with apatite are subject to chlorine attack, and thereby become sensitive. Local deterioration of chromium oxide layer that formed on the surface [37] results in weight loss, and thus increases corrosion rates.





Figure 10. SEM images taken from base metal, HAZ and weld metal from (a) and (b) B1, (c) macro image, (d), (e) and (f) HAZ from B2 heat treated samples immersed in SBF for 28 days.

After cleaning with nitric acid solution (HNO₃) to remove corrosion products that could be produced on the surface of laser welded samples immersed in SBF for 28 days, SEM-EDS examinations were carried out, and the images are given in Figure 10 and 11. No formation indicating corrosion mechanisms were observed on base metal, HAZ, and weld metal of B1 sample (Figure 10 (a) and (b). EDS analysis showed that amount of chromium in B1 sample was higher than that in B2 sample. However, an examination of SEM images of B2 sample which was joined using a higher heat input did not reveal any corrosion or crack in base metal and weld metal, but indicated that a complete dissolution occurred in HAZ, chromium oxide layer was locally disrupted, and an intense corrosion mechanism took place.

Corrosion development could be due to chromium carbide or nitride forming around HAZ in addition to microsegregation, which occurred in heat treatment conditions. Results of EDS analysis (Figure 11) showed that chromium ratio in corrosion zone of HAZ increased considerably compared to corrosion forming on base metal or on weld metal. Excessive chromium amount in corrosion region in fact represents the local content in chromium oxide layer dissolved in the surface of sample and should not be confused with general chromium content of material structure. Observation of chromium carbide or nitride formations especially in HAZ in optical microscope, and SEM-EDS, mapping analysis of samples before the corrosion test should be evaluated as an indication that these regions could have sensitivity against corrosion. It is well known that corrosion starts in the regions where these formations are located, and spreads rapidly.

Weaker corrosion resistance has been observed in the sample, which is joined with high heat input due to more accumulation of large-sized carbides in the grain boundaries and softened microstructure. It is important to note that large-sized carbides reduce corrosion resistance more than small carbides [38]. Isfahany et al who investigate the properties of electrochemical corrosion of heat treated martensitic stainless steel suggest that there is an influence of the dissolution of alloying elements, such as chromium and carbon in the microstructure on the behavior of the corrosion of martensitic stainless steel and they suggest that the degradation of chromium oxide passive film layer on surfaces supports corrosion resistance [39]. The amount of passivating elements has an effect on the corrosion resistance of AISI 420 martensitic stainless steel [40]. This study also suggests that the

properties of passive film that occurs on the surface of martensitic stainless steel has the most important effect on the corrosion resistance.



Figure 11. EDS point analysis of base metal, HAZ and weld metal from (a) B1, (b) B2 heat treated samples immersed in SBF for 28 days.

4. CONCLUSION

• Microstructure of non-heat treated laser welded sample was predominantly made up martensitic phase. Microstructure of heat treated laser welded sample, on the other hand, made up tempered martensite, small amount of ferrite and little amounts of carbides.

• EDS point analysis on heat treated base metal, HAZ, and weld metal immersed in SBF and elemental mapping analysis of weld metal revealed a decrease of especially chromium element. Depending upon heat treatment process, chromium produced carbides, such as $Cr_{23}C_6$, $M_{23}C_6$, and led to local Cr decreases, causing corrosion sensitivity. In addition, weld heat input affected the corrosion resistance.

• Based on SEM imaging of surfaces of all samples immersed in SBF, apatite development was more pronounced on heat treated base metal surface compared to heat treated laser welded samples. This finding could be explained by better bioactive properties of base metal compared to welding seam of laser welded samples. EDS point analysis results of apatite covered base metal surface and welding seam of laser welded showed Ca/P ratios of lower than 1.67, stoichiometric value of bone. Surface of all samples were covered with apatite minerals called calcium deficient carbonate hydroxyapatite structure with low crystallinity.

• It was concluded that heat treated base metal and laser welded samples of AISI 420 stainless steel using different two welding speeds had corrosion rates higher than the tolerable corrosion rate to be used as an implant inside human body. These results strongly support the idea that heat treated base metal and laser welded AISI 420 martensitic stainless steel cannot be used as temporary or permanent implant in human body. However, results with this material could be improved using various surface treatment methods.

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References

- 1. S. Kou, Welding Metallurgy, 2th ed. A John Wiley & Sons INC, New Jersey (2003).
- 2. J.R. Davis, *Stainless Steels*, ASM international, Materials Park, Ohio (1994).
- 3. B. Kurt, N. Orhan, I. Somunkıran I, and M. Kaya, Mater. Des., 30 (2009) 661.
- 4. T. Iamboliev, *W&MT*, 4 (2015) 1.
- 5. P. Bilmes, C. Llorente, and J.P. Ipina, J. Mater. Eng. Perform., 9 (2000) 609.
- 6. C. Köse, and R. Kaçar, Mater. Des., 64 (2014) 226.
- 7. S.M. Manhabosco, Á.P. dos Santos, M.L. Marcolin, E.F. Pieretti, M.D.M. Neves, and L.F.P. Dick, *Electrochim. Acta*, 200 (2016) 189.
- 8. C. Köse, and R. Kaçar, NWSA Technol. Appl. Sci., 10 (2015) 13.
- 9. N. Katı, and S. Ozan, Mater. Test., 58 (2016) 747.
- 10. ISO 7153-1, Surgical instruments-Metallic Materials-Part 1-Stainless Steel, ISO, UK (2014).
- 11. A. Okada, Y. Uno, J.A. McGeough, K. Fujiwara, K. Doi, K. Uemura, and S. Sano, CIRP Ann. Manuf. Technol., 57 (2008) 226.
- 12. J.O. Nilsson, J. Phys., 3 (1993) 67.
- 13. I. Gurappa, Mater. Charact., 49 (2002) 79.
- 14. D.A. Lopez, A. Duran, and S.M. Cere, J. Mater. Sci.: Mater. Med., 19 (2007) 2137.
- 15. C. Köse, and R. Kaçar, Mater. Test., 56 (2014) 785.

- 16. C. Köse, and R. Kaçar, J. Fac. Eng. Archit. Gaz., 3 (2015) 225.
- 17. C. Köse, R. Kaçar, A.P. Zorba, M. Bağırova, and A.M. Allahverdiyev, *Mater. Sci. Eng., C*, 60 (2016) 211.
- 18. C. Köse, and R. Kaçar, Int. J. Electrochem. Sci., 11 (2016) 2762.
- 19. C. Köse, Int. J. Electrochem. Sci., 11 (2016) 3542.
- 20. C. Köse, Mater. Test., 58 (2016) 963.
- 21. C. Köse, and E. Karaca, Arch. Metall. Mater., 63 (2018) 1225.
- 22. R.O. Uzun, and Ö. Keleş Ö, J. Fac. Eng. Archit. Gaz., 27 (2012) 509.
- 23. C. Köse, and E. Karaca, Metals, 7 (2017) 1.
- 24. ASTM G1-03-E, Standard Practice for Preparing, Cleaning, and Evaluation Corrosion Test Specimens, American Society for Testing and Materials (1999).
- 25. T. Kokubo, and H. Takadama, Biomaterials, 27 (2006) 2915.
- 26. R. Yilmaz, and A. Türkyilmazoglu, Adv. Mat. Res., 23 (2007) 319.
- 27. J.A. Disegi, and L. Eschbach, Injury, 31 (2000) 2.
- 28. A. Zadpoor, Mater. Sci. Eng., C, 35 (2014) 143.
- 29. S.L. Aktuğ, S. Durdu, E. Yalçın, K. Çavuşoğlu, and M. Usta, Mater. Sci. Eng., C, 71 (2017) 1020.
- 30. M. Dinçer, D. Teker, P. Sağ Can, and K. Öztürk, Surf. Coat. Tech., 226 (2013) 33.
- 31. X. Fan, J. Chen, J.P. Zou, Q. Wan, Z.C. Zhou, and J.M. Ruan, *Trans. Nonferrous Met. Soc. China*, 19 (2009) 352.
- 32. K. Byrappa, and T. Ohachi, *Crystal Growth Technology*, *Cheapter 16, Growth of Hydroxyapatite Crystals*-Atsuo Ito and Kazuo Onuma, William Andrew Publishing, NewYork (2006).
- J. Ballarre, I. Manjubala, W.H. Schreiner, J.C. Orellano, P. Fratzl, and S. Ceré, *Acta. Biomater.*, 6 (2010) 1609.
- 34. G. Manivasagam, D. Dhinasekaran, and A. Rajamanickam, *Recent Patents on Corros. Sci.*, *Bentham Open*, 2 (2010) 54.
- 35. K.K. Chew, S.H.S. Zein, and A.L. Ahmad, Nat. Sci., 4 (2012) 184.
- 36. D.C. Hansen, *Electrochem. Soc. Interface*, 17 (2008) 31.
- 37. E.F. Pieretti, and I. Costa, *Electrochim. Acta*, 114 (2013) 838.
- 38. C.T. Kwok, K.H. Lo, F.T. Cheng, and H.C. Man, Surf. Coat. Tech., 166 (2003) 221.
- 39. A.N. Isfahany, H. Saghafian, and G. Borhani, J. Alloys Compd., 509 (2011) 3931.
- 40. B. Mahmoudi, M.J. Torkamany, A.R. Sabour Rouh Aghdam, and J. Sabbaghzadeb, *Mater. Des.*, 31 (2010) 2553.

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