Bitlis Eren University Journal of Science
BİTLİS EREN ÜNİVERSİTESİ FEN BİLİMLERİ DERGİSİ
ISSN: 2147-3129/e-ISSN: 2147-3188
VOLUME: 11 NO: 1 PAGE: 71-78 YEAR: 2022
DOI: 10.17798/bitlisfen.994657

Combined Effect of Cryogenic and Aging Treatments on Wear Behavior of Ti-6Al-4V α/β Alloy for Biomedical Applications

Nihal YUMAK[1]*

[1]*Department of Mechanical Engineering, Afyon Kocatepe University,*
Gazlıgol Rd., Afyon, 03200, TURKEY
(ORCID: 0000-0003-4492-7142)

Keywords: Ti-6Al-4V titanium alloy, α/β alloy, Cryogenic treatment, Aging treatment, Wear.

Abstract
Ti-6Al-4V α/β titanium alloy is used in the biomedical industry to produce artificial joints due to its excellent osseointegration property, low density, and low Elasticity modulus compatible with bone structure. Ti-6Al-4V alloy is expected to have high wear resistance to prevent toxic elements such as Al, V from being released into the body environment during joint movement. In this study, aging treatment and a combination of aging and cryogenic treatment were applied to the alloy to obtain advanced tensile properties and wear resistance. Cryogenic treatments were conducted at deep (-196°C) and shallow (-140°C) cryogenic treatment temperatures. After that, single-step and duplex aging treatment were conducted to the one group of samples after the cryogenic treatment, while another group was single-step and duplex aged without cryo treatment. The heat treatments' influence on the alloy's tensile, wear, and microstructural properties were determined by tensile, wear tests, XRD phase analysis, and microstructural investigations. After applying the duplex aging treatment amount of the β phases decreased, a good balance between tensile strength and the elongation was obtained, and the wear resistance of the alloy increased compare to the single-step aging. In addition, the decrease of the cryogenic treatment temperature slowed down the phase transformation kinetics, and it caused a decrease in precipitation of α phases at both single-step and duplex aged samples. Superior wear resistance was obtained with the decreasing of β phases in the microstructure of the samples that were duplex aged after cryogenic treatment.

1. Introduction

Ti-6Al-4V alloy, also known as Ti 6-4, was developed firstly for use in the aerospace industry in the 1950s [1]. However, nowadays, Ti 6-4 alloy is highly used in the biomedical sector in orthopedics implant applications [2]. Ti 6-4 alloy is an ideal material for long-term use, thanks to its excellent biocompatibility, high strength, and high fatigue strength compared to commonly used materials in biomedical applications such as cobalt-based alloys and stainless steel [3]. However, recent studies in the literature revealed that Ti 6-4 alloy could be induced Alzheimer's diseases because of the Al and V elements toxic effects [4]. Ti 6-4 alloy′s low tribological behavior could cause the release of Al and V elements. The wear resistance of the Ti 6-4 alloy that is widely used at artificial joints is needed for detailed investigation and enhancement when considering this discovery. In addition, the alloy is expected to have high tensile properties to work safely under the loads it is exposed to in the field of use. Studies have recently been made that marked improvement of the alloy's impact behavior, fatigue strength, and tensile strength was obtained by applying the heat and thermomechanical treatments[5]–[7]. Nevertheless, keeping a good balance between the tensile strength and elongation and getting advanced wear resistance is still challenging.

Cryogenic treatment traditionally is applied to the tool steel to transform retained austenite to martensite, precipitate the fine carbide, and eliminate residual stress [8]. Recently, the cryogenic

---

*Corresponding author: nyumak@aku.edu.tr

Received: 13.09.2021, Accepted: 30.11.2021

treatment has been widely used to improve the vibration damping capacity of rotating shafts[9]–[12]. Studies have shown that the damping ability of AISI 4140 steel increased significantly after deep cryogenic treatment. However, in the literature review, studies that cryogenic treatment conducted to the titanium alloy's were also found. These studies concentrated on the cryogenic treatment effect on the titanium alloy's low-velocity impact behavior [7], fatigue crack propagation behavior [13], and fracture toughness [14]. Cryogenic treatment could be conducted at two temperatures range as shallow between the -80°C and -160°C (193–113K) and deep between the -160°C and -196°C (113–77K) cryogenic treatment [15]. In the study made by Senthilkumar et al., it was obtained that deep cryogenic treatment generates more compressive residual stress compared to the shallow cryogenic treatment [16]. The residual stress generated during cryogenic treatment determined the alloy's tensile properties and hardness. The wear resistance of the Ti 6-4 alloy, which was the cryo treated at different temperatures (-80°C, -140°C, and -196°C), was studied by Gu et al.[17]. The study showed that wear resistance improved with the reduction of the cryogenic treatment temperature thanks to the diminished of the β phase volume fraction and the grain refinement. Aging treatment is another heat treatment type applied with different treatment steps and parameters to the titanium alloys with/without cryogenic treatment [4]. Mainly, multi-step aging treatments have been applied to the titanium alloy lately with satisfying results [18]. Junior and Correa studied the effect of the two-step aging treatment on the Ti 6-4 alloy stress corrosion cracking behavior [19]. Decomposing the β phases by applying the two-step aging treatment improved the Ti 6-4 alloy's stress corrosion cracking behavior.

As seen in the literature review, studies investigating the mechanical strength of the Ti 6-4 alloy by applying the cryogenic treatment with/without aging treatment have been made [12, 15]. However, the influence of the multi-step aging combined with cryogenic treatment on the Ti 6-4 alloy's tensile properties and wear behavior has been under-considered. Therefore, the authors applied shallow and deep temperature cryogenic treatment to Ti 6-4 alloy followed by a single-step and duplex aging treatment to examine the Ti 6-4 alloy's microstructural and tensile properties and wear behavior.

2. Material and Method

Ti 6-4 α/β alloy was supplied as annealed and plate form (2000x2000x2 mm). The annealed sample' tensile test results were given in another study conducted by the author [7]. Ti 6-4 α/β titanium alloy′s chemical composition is given in the Table I.

Table 1. The chemical compositions of Ti 6-4 alloy (wt %)

Weight	Al	V	C	Fe	O	Ti
Ti 6-4	6.7	3.83	0.08	0.03	0.2	Balance

2.1. Application of the Cryogenic and Aging Treatment Steps

Cryogenic treatment was carried out in the cryogenic tank, which is cooled down to the cryogenic temperatures via a computer control system using nitrogen. In this study, cryogenic treatment was conducted to the alloy at shallow and deep cryogenic treatment temperatures. Deep cryo treatment was conducted on the samples at -196°C for 24 hours. Also, shallow cryo treatment was applied to the samples at -140°C for 6 hours. The cooling/heating rate was 2ºC/minute. Single-step and duplex aging treatments were conducted to the Ti 6-4 titanium alloy with or without cryo treatment. Single-step aging treatment was conducted on the samples at 600°C for 1 hour. Duplex aging was applied with an extra aging treatment step on the single-step aging treatments. During duplex aging treatments, samples were first aged at 600°C for 1 hour, and then an extra aging step was applied at 400°C for 1 hour. The detail of the treatment temperature, time, and the samples' coding system are shown in Table 2. Also, a schematic presentation of heat treatment steps is shown in Figure 1.

2.2. Microstructural Observations and Mechanical Tests

Microstructural analysis was made via scanning electron microscope (SEM) and XRD analyses. Heat-treated samples were ground with abrasive papers (800, 1000, and 1200 mesh numbers) and were polished 1μm alumina solution. After that, Kroll solution (5% HF, 10% HNO_3, and 85% distilled H_2O) was used for etching to heat-treated samples. The solution was applied to the samples for 25 s

Table 2. Heat-treated sample groups and coding system

Coding System	**Heat treatment temperature and time**					
	Cryogenic treatment		**Pre-aging**		**Second-step aging**	
	Temperature(°C)	*Time(h)*	*Temperature(°C)*	*Time(h)*	*Temperature(°C)*	*Time(h)*
S	-	-	600	1	-	-
D	-	-	600	1	400	1
C_1S	-140	6	600	1	-	-
C_1D	-140	6	600	1	400	1
C_2S	-196	24	600	1	-	-
C_2D	-196	24	600	1	400	1

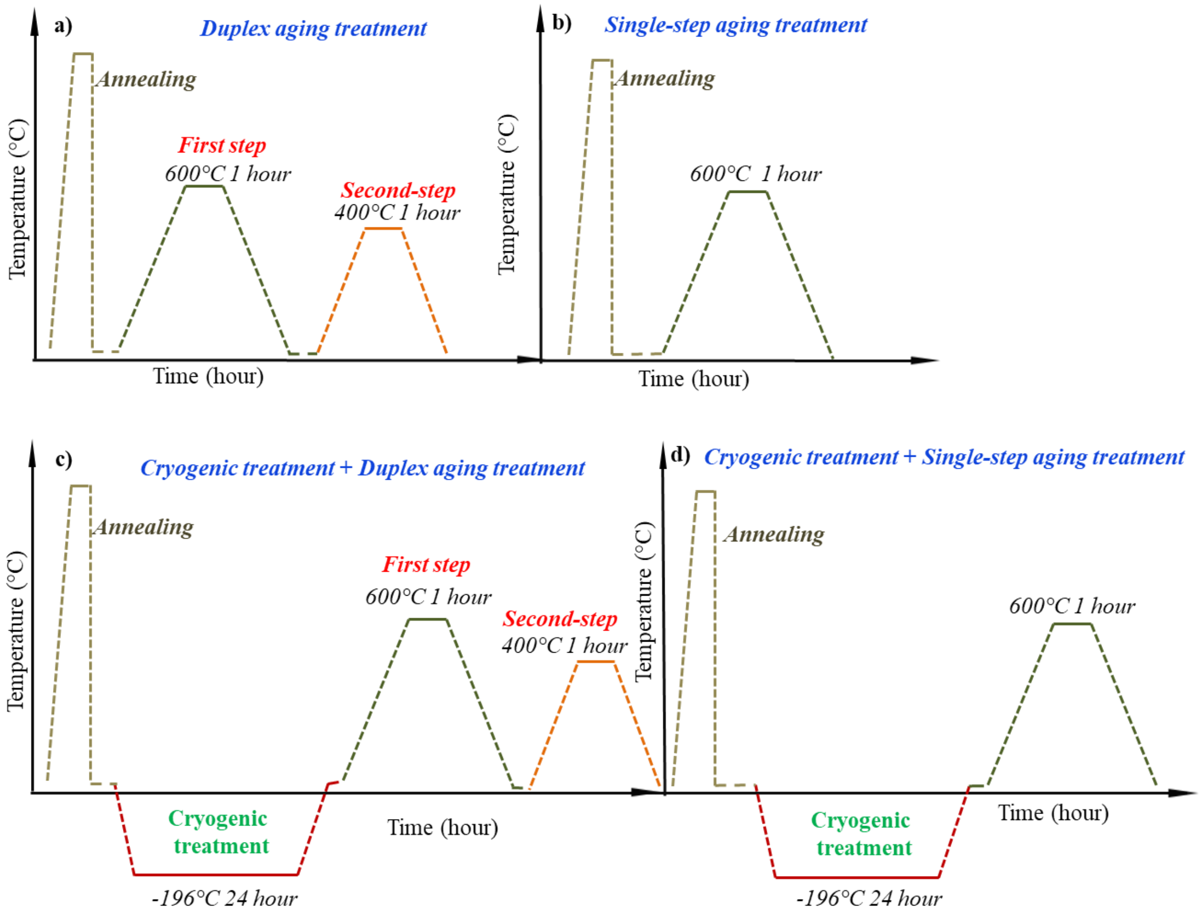

Figure 1. Schematic presentation of heat treatment steps, a) Sample D, b) Sample S c) Sample C_2D, d) Sample C_2S

Tensile tests were applied with the Instron brand tensile test device according to the ASTM E8-04 with a 1 mm/min loading rate. Vickers hardness tests were applied under a 100g load, and the tests were repeated ten times for each sample. XRD analyses were performed on the heat-treated samples with Bruker Model diffractometer with a 2.2 KW Cu anode, Nickel filter, (scanning rate was 1°/min, 2θ was scanned between 30-90°). The wear resistance of the samples was evaluated under dry sliding conditions by pin-on-disk test. The sliding distance was 100 meters, the load was 5N, and the sliding velocity was 0.25 m/s. The coefficients of friction were recorded during tests, and mass loss of the wear test samples was determined by measuring the test samples' weight before and after the test. After the wear tests, wear traces were observed with the LEO 1430 VP model SEM.

3. Result and Discussion

3.1. Microstructural Analysis

During cryogenic treatment, Ti 6-4 alloy is cooled to subzero temperatures; therefore, the vanadium content of the β phases diminishes, and metastable β phases transform into the β_{lean} and β_{rich} phases. The β_{lean} and β_{rich} phases transform at the end of the cryogenic treatment to ($\beta_{lean}\rightarrow\beta$) β and ($\beta_{rich}\rightarrow\alpha$) α phases[21]. Completing the transformation sequences causes a decrease in the quantity of β phases in the cryo-treated Ti 6-4 alloy microstructure[17]. Similarly, in this study, the application of cryogenic treatment caused a decreased quantity of β phases at the Ti 6-4 microstructure. As seen from Figure 2, β phases amount decreased in samples that were aged after cryogenic treatment compared to the aged samples. Also, it is known that metastable phases (α′, α″, β) can transform into β and α phases after aging treatment[22]. Likewise, in the duplex aged sample, these phase formations increased with the applied second step aging treatment, and the quantity of β phases decreased more than in the single-step aged sample. Thus, a noticeable increase in the α phases was found after the duplex aging treatment. After the cryo treatment, this phase precipitation tendency did not change with one exception. The samples that were cryo-treated at -140°C for 6 hours before single-step aging treatment was the exception. C_1S sample′s amount of α phases was found higher than C_1D sample. With the reduction of the cryogenic treatment temperature to -196°C from -140°C, phase transformation kinetics decreased since the movement of the atoms slowed down[17]. As can be seen in Figure 2, the ratio of α phases decreased.

XRD analysis of the heat-treated samples demonstrated that new phases were not formed after the aging or cryogenic treatments. However, phases intensity changed with the application of the heat treatment steps. As can be seen from Figure 3a, α phases peak intensity increased obviously with the application of cryogenic treatment at -140°C for 6 hours at 2θ~40 and 2θ~70. Compared to the C_2S, α phases peak intensity increased at C_1S after increasing the cryo treatment temperature because of the slow down of the phase transformation kinetics at low cryogenic temperatures. The same tendency was acquired in the duplex-aged samples after the cryogenic treatment (Figure 3b). Also, the application of the second-step aging treatment after the single-step aging treatment, α phases peak intensity incremented as against the single-step aged samples.

3.2. Tensile and Microhardness Test Results

Microhardness test results show that the hardness of the duplex aged samples was lower than the single-step aged samples. This tendency continued in the same way in the samples that were aged after the cryogenic treatment. For this reason, the highest hardness value was obtained as 460 HV in the single-step aged sample, while the lowest hardness value was obtained as 441 HV in the duplex aged sample after shallow cryogenic treatment. As a result, the hardness decreased by 4% with cryogenic and duplex aging treatment in the C_1D sample compared to the single-step aged sample. Another remarkable issue in the test results is that the hardness increased with the decreasing the cryo processing temperature.

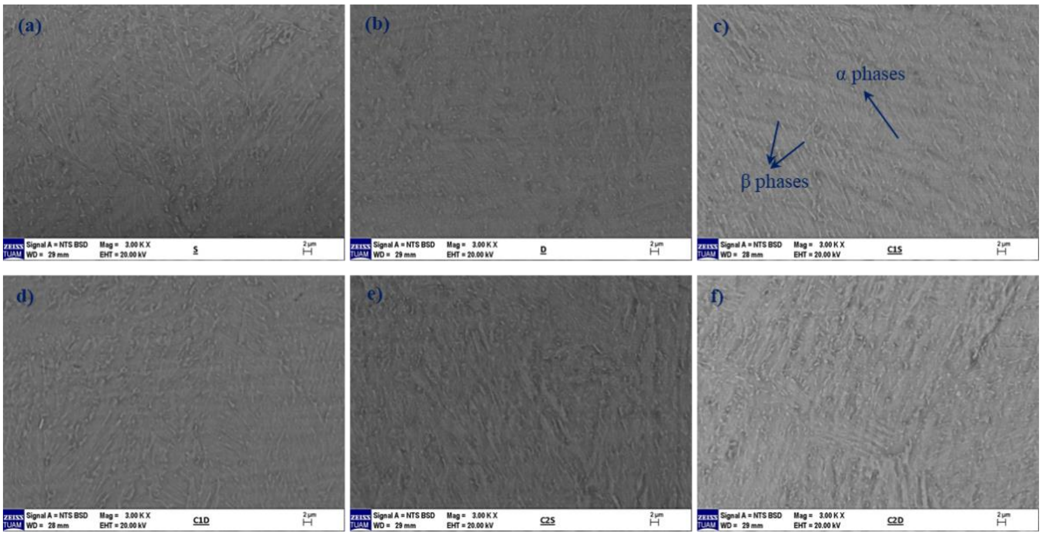

Figure 2. Microstructure images of the heat-treated samples, a) Sample S, b) Sample D, c) Sample C_1S, d) Sample C_1D, e) Sample C_2S, f) Sample C_2D

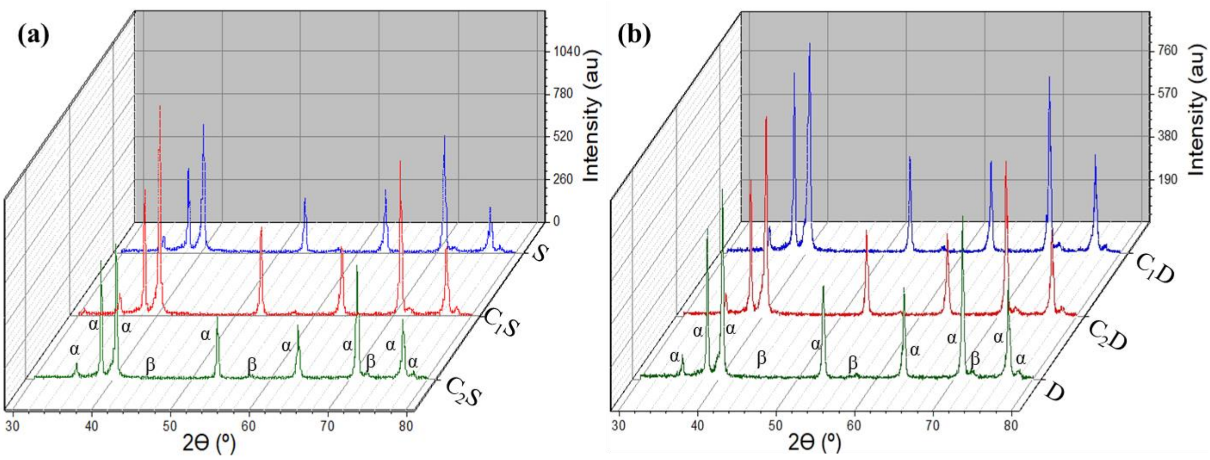

Figure 3. XRD phase analysis, a) S, C_1S, C_2S samples, b) D, C_1D, C_2D samples

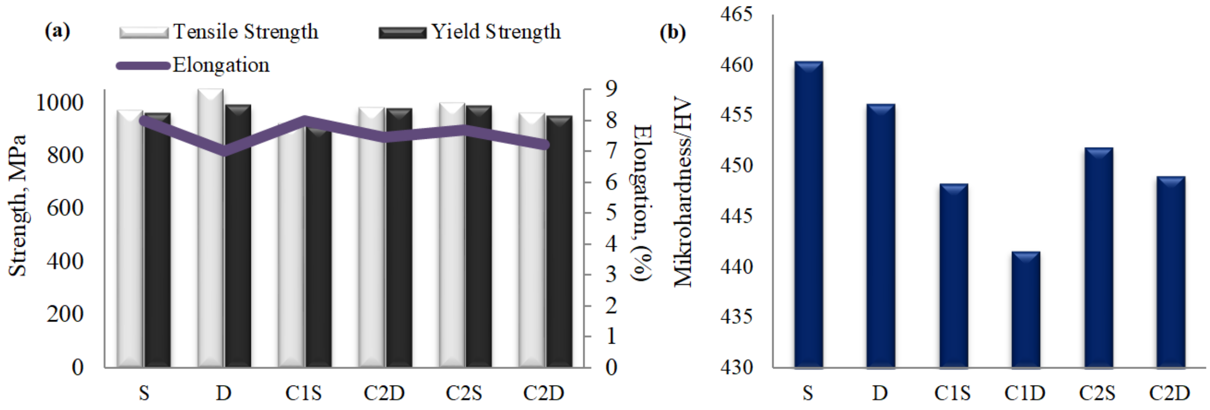

Figure 4. Heat-treated samples tensile and hardness test results, a) Tensile test results, b) Hardness test results

As can be seen, with the decrease in cryogenic temperature from -140°C to -196°C, the hardness of both single-step and duplex aged samples increased. The tensile test results of the samples show that duplex aging treatment increased the tensile and yield strength of the alloy as against the single-step aging treatment. Nevertheless, duplex aging treatments have a negative impact on the elongation of the Ti 6-4 alloy. Also, with the application of the cryo treatment, tensile strength decreased, and elongation increased slightly in both single-step and duplex-aged samples.

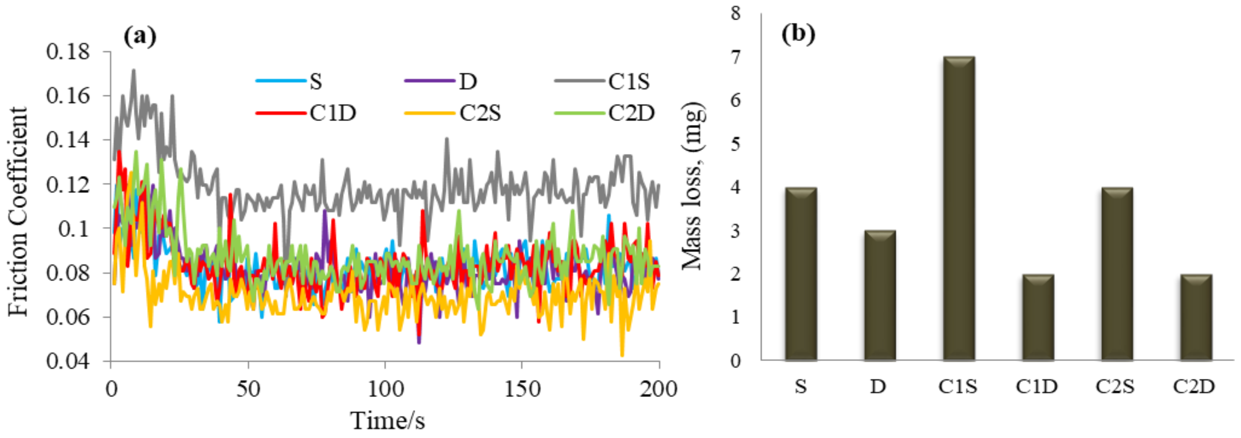

Figure 5. Wear test results of heat-treated samples, a) Comparison of friction coefficients, b) Mass loss value in heat-treated wear test samples

3.3. Wear Tests Results

As can be seen from Figure 5, the wear resistance increased, and the mass loss decreased due to the decreasing β phases in the microstructure with the application of duplex aging treatment as against the single-step aging treatment. Similar results were observed in duplex-aged samples after cryogenic treatment too. Another result obtained from the wear tests is that, as a result of the decrease of β phases after the cryo treatment, the wear resistance was found to be higher than the only aged samples. The increase in wear resistance after cryogenic treatment was explained by the decrease of β phases, high dislocation density, and the formation of twinning in the literatüre [17]. The decrease of the cryogenic treatment temperature to -196°C increased the wear resistance and caused the reduction of the mass loss after the wear tests. However, the wear resistance decreased with the increase of the cryogenic treatment temperature, and the highest friction coefficient was obtained in the C1S sample.

Worn surfaces are shown in Figure 6 of the heat-treated samples. As seen in Figure 6a-b, smoother surfaces were obtained at the duplex aged sample against the single-step aged sample. However, in the C1S secondary crack occurred on the worn surfaces because of the decrease of the wear resistance (Fig. 6c). On the other hand, the wear resistance increased, and the secondary cracks on the surface disappeared in the sample, in which the duplex aging process was applied after the shallow cryogenic treatment (Fig. 6d).

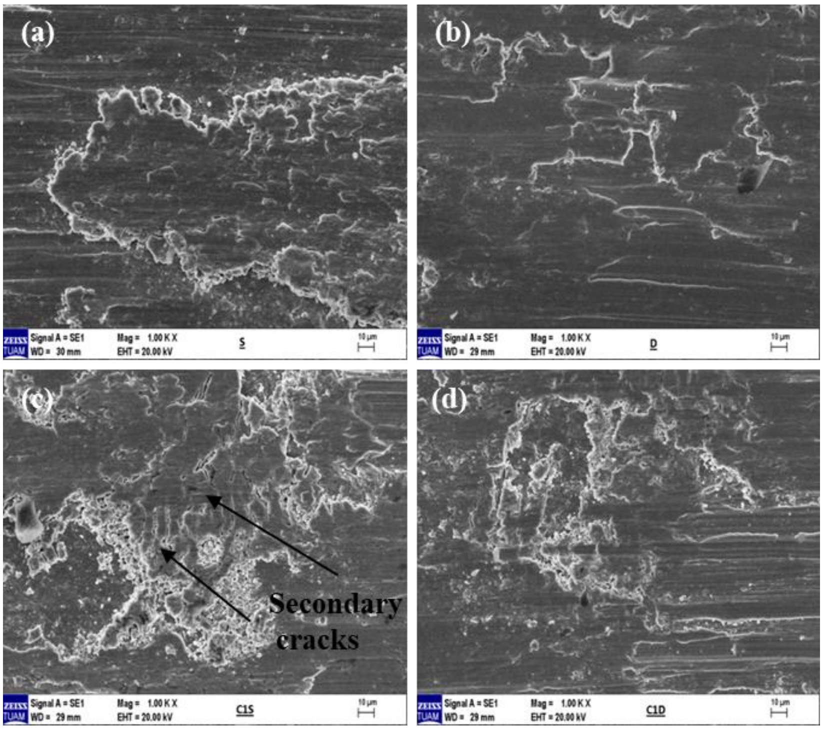

Figure 6. Worn surfaces analysis, a) S, b) D, c) C_1S, d) C_1D

4. Conclusion

Ti 6-4 titanium alloy is used in the biomedical industry due to its high fatigue strength, tensile properties, and low Elasticity modulus. However, some studies recently published in the literature have shown that elements such as Al and V may be released due to the low wear resistance of the alloy and that the use of the alloy in the long term may cause diseases such as Alzheimer's. In this study, aging treatment and a combination of aging and cryogenic treatment were applied to the alloy to obtain high tensile properties and wear resistance. Cryogenic treatments were conducted at deep (-196°C) and shallow (-140°C) cryogenic treatment temperatures. Also, the alloy was aged with/without cryogenic treatment as a single-step or duplex. Heat treatment steps' effect on the tensile and wear properties of the alloy were investigated in detail. Some significant conclusions obtained from the study were listed as follows;

- Duplex aging treatment increased the α phase volumetric fraction, a good balance between tensile strength and elongation was obtained in comparison with the single-step aging treated samples.

- The decrease of cryogenic treatment temperature slowed down the phase transformation kinetics and caused a decrease in precipitation of α phases at both single-step and duplex aged samples. The highest hardness was measured in the single-step aged sample, while the lowest hardness value was obtained in the duplex aged sample after shallow cryogenic treatment.
- Superior wear resistance was obtained with the reduction of β phase quantity in the samples that were duplex aged after cryogenic treatment.

Statement of Research and Publication Ethics

Research and publication ethics were complied with in the study.

References

[1] K. Prasad et al., “Metallic Biomaterials: Current Challenges and Opportunities,” Mater. 2017, Vol. 10, Page 884, vol. 10, no. 8, p. 884, Jul. 2017, doi: 10.3390/MA10080884.

[2] C. dVeiga, J. Davim, and A. Loureiro, “Properties and applications of titanium alloys: a brief review,” Rev. Adv. Mater. Sci, vol. 32, no. 2, pp. 133–148, 2012.

[3] W. S. W. Harun, M. S. I. N. Kamariah, N. Muhamad, S. A. C. Ghani, F. Ahmad, and Z. Mohamed, “A review of powder additive manufacturing processes for metallic biomaterials,” Powder Technol., vol. 327, pp. 128–151, Mar. 2018, doi: 10.1016/j.powtec.2017.12.058.

[4] N. Yumak and K. Aslantas, “A review on heat treatment efficiency in metastable b titanium alloys: The role of treatment process and parameters,” J. Mater. Res. Technol., vol. 9, no. 6, pp. 15360–16280, Nov. 2020, doi: 10.1016/j.jmrt.2020.10.088.

[5] N. Yumak and K. Aslantas, “Effect of notch orientation and single overload on crack interaction in Ti–6Al–4V alloy,” J. Brazilian Soc. Mech. Sci. Eng., vol. 41, no. 8, Aug. 2019, doi: 10.1007/s40430-019-1816-6.

[6] R. Ding, Z. X. Guo, and A. Wilson, “Microstructural evolution of a Ti–6Al–4V alloy during thermomechanical processing,” Mater. Sci. Eng. A, vol. 327, no. 2, pp. 233–245, Apr. 2002, doi: 10.1016/s0921-5093(01)01531-3.

[7] N. Yumak, K. Aslantas, and Y. Pekbey, “Effect of cryogenic and aging treatments on low-energy impact behaviour of Ti–6Al–4V alloy,” Trans. Nonferrous Met. Soc. China (English Ed., vol. 27, no. 3, pp. 514–526, Mar. 2017, doi: 10.1016/s1003-6326(17)60058-x.

[8] P. Baldissera and C. Delprete, “Deep Cryogenic Treatment: A Bibliographic Review,” Open Mech. Eng. J., vol. 2, no. 1, pp. 1–11, Jan. 2008, doi: 10.2174/1874155x00802010001.

[9] M. Kam and H. Saruhan, “Vibration damping capacity of deep cryogenic treated AISI 4140 steel shaft supported by rolling element bearings,” Mater. Test., vol. 63, no. 8, pp. 742–747, Aug. 2021, doi: 10.1515/mt-2020-0118.

[10] M. Kam, H. Saruhan, U. Kabasakaloglu, and T. Guney, “Vibration damping capacity of a rotating shaft heat treated by various procedures,” Mater. Test., vol. 63, no. 10, pp. 966–969, Oct. 2021, doi: 10.1515/mt-2021-0026.

[11] Menderes Kam, Hamit Saruhan, And Ufuk Kabasakaloğlu, “Experımental Investıgatıon Of Vıbratıon Generated From The Cryogenıc Treated And Inductıon Surface Hardened Rotatıng Shafts,” in 3 rd International Symposium on Railway Systems Engineering (ISERSE’16), Sep. 2016, pp. 142–148, Accessed: Nov. 03, 2021.

[12] M. Kam and H. Saruhan, “Experımental Vıbratıon Analysıs Of Cryogenıc Treated Rotatıng Aısı 4140 Steel Shafts,” in 3 rd International Symposium on Railway Systems Engineering (ISERSE’16), 2016, vol. 3, pp. 157–164, Accessed: Nov. 03, 2021.

[13] A. K. Singla et al., “Impact of Cryogenic Treatment on HCF and FCP Performance of β-Solution Treated Ti-6Al-4V ELI Biomaterial,” Mater. 2020, Vol. 13, Page 500, vol. 13, no. 3, p. 500, Jan. 2020, doi: 10.3390/ma13030500.

[14] K. Nagai, T. Yuri, O. Umezawa, and K. Ishikawa, “Fatigue and Fracture of Ti Alloys at Cryogenic Temperatures,” in 11th International Conference on Magnet Technology (MT-11), Springer Netherlands, 1990, pp. 754–759.

[15] D. Das, A. K. Dutta, and K. K. Ray, “Sub-zero treatments of AISI D2 steel: Part II. Wear behavior,” Mater. Sci. Eng. A, vol. 527, no. 9, pp. 2194–2206, Apr. 2010, doi: 10.1016/j.msea.2009.10.071.

[16] D. Senthilkumar, I. Rajendran, M. Pellizzari, and J. Siiriainen, “Influence of shallow and deep cryogenic treatment on the residual state of stress of 4140 steel,” J. Mater. Process. Technol., vol. 211, no. 3, pp. 396–401, Mar. 2011, doi: 10.1016/j.jmatprotec.2010.10.018.

[17] K. Gu, J. Wang, and Y. Zhou, “Effect of cryogenic treatment on wear resistance of Ti-6Al-4V alloy for biomedical applications,” J. Mech. Behav. Biomed. Mater., vol. 30, pp. 131–139, Feb. 2014, doi: 10.1016/j.jmbbm.2013.11.003.

[18] N. Yumak and K. Aslantas, “Effect of Heat Treatment Procedure on Mechanical Properties of Ti-15V-3Al-3Sn-3Cr Metastable β Titanium Alloy,” J. Mater. Eng. Perform., pp. 1–9, 2021, Accessed: Jan. 12, 2021.

[19] P. C. P. Santos and E. O. Correa, “Effect of Duplex Aging Heat Treatment on the Stress Corrosion Cracking Behavior of Ti-6Al-4V α+β Titanium Alloy in Methanol,” Mater. Res., vol. 24, no. 3, p. 20200456, May 2021, doi: 10.1590/1980-5373-MR-2020-0456.

[20] N. Yumak, K. Aslantaş, and A. Çetkin, “Cryogenic and Aging Treatment Effects on the Mechanical Properties of Ti-15V-3Al-3Cr-3Sn Titanium Alloy,” J. Test. Eval., vol. 49, no. 5, 2020,

[21] K. Gu, H. Zhang, B. Zhao, J. Wang, Y. Zhou, and Z. Li, “Effect of cryogenic treatment and aging treatment on the tensile properties and microstructure of Ti-6Al-4V alloy,” Mater. Sci. Eng. A, vol. 584, pp. 170–176, Nov. 2013, doi: 10.1016/j.msea.2013.07.021.

[22] L. Zeng and T. R. Bieler, “Effects of working, heat treatment, and aging on microstructural evolution and crystallographic texture of α, α′, α″ and β phases in Ti–6Al–4V wire,” Mater. Sci. Eng. A, vol. 392, no. 1–2, pp. 403–414, Feb. 2005, doi: 10.1016/J.MSEA.2004.09.072.