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# Oxidation resistance of titanium alloys at high temperatures

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**Abstract.** In the present work, the oxidation resistance of a titanium-aluminium alloy after annealing for one hour at temperatures of 300, 500, 700 and 900 °C was investigated. It was found that the alloy had the best mechanical and tribological properties after annealing at 700 °C. Oxide film flaking after annealing at 900 °C was observed as well.

**Keywords:** titanium-aluminium alloy, annealing, oxidation, microhardness, friction coefficient, wear resistance, TC25.

## 1. Introduction

Alloys of the Ti-Al-V-Zr-Mo system are among the most commonly used titanium alloys due to their optimal complex mechanical properties [1]. However, the principal disadvantage of titanium is its high tendency to absorb oxygen at temperatures exceeding 500 °C, which leads to surface embrittlement. The development of methods for modifying Ti-Al alloys with an operating temperature of more than 600 °C represents an urgent task, as it would allow the range of applications for titanium alloys to be expanded. Therefore, it's important that we get a better understanding of how titanium alloys are oxidized if we want to make further progress.

## 2. Materials and Methods

The object of this study was an alloy TC25 comprising titanium and aluminium. The elemental composition of the alloy prior to heat treatment is presented in Table 1.

The alloy was subjected to one-hour annealings in a muffle furnace at temperatures of $T$ = {300, 500, 700, 900} °C. Then, phase analysis was carried out using X-ray diffraction (XRD) (Ridaku UltimaIV, theta-2theta, $\lambda = 0.154050$ nm), changes in elemental composition were recorded using energy-dispersive X-ray spectroscopy (EDX). Microhardness measurements were carried out using a microhardness tester MVD402 Wolpert Wilson Instrument (Vickers method, load $P$ = {0.49, 0.98} N), the tribology of the alloy was studied in the dry friction mode (load $P$ = 0.49 N, sample velocity 4 mm/s). The tracks obtained were investigated by profilometer 3002 SD26-SN3049.

## 3. Results and Discussion

### *3.1. Energy-dispersive X-ray spectroscopy*

Table 1 illustrates that the composition of alloy TC25 is Ti-83.4Al-12.6V-2.1Zr-1.2Mo-0.7 at. %. The primary alloying element present in the TC25 alloy is aluminium. The concentration of other alloying elements does not exceed 2.1 at. %.

**Table 1.** Elemental composition of the TC25 alloy before heat treatment and after one-hour annealing at T = {300, 500, 700, 900} °C.

| *T*, °C | *Elemental composition, at. %* | | | | | |
|---|---|---|---|---|---|---|
| | Ti | Al | V | Zr | Mo | O |
| 24 | 83.4 | 12.6 | 2.1 | 1.2 | 0.7 | – |
| 300 | 75.5 | 8.9 | 1.7 | 1.0 | 0.7 | 12.2 |
| 500 | 60.6 | 7.7 | 1.3 | 0.8 | 0.6 | 29.0 |
| 700 | 49.9 | 6.1 | 0.6 | 0.7 | 0.6 | 42.1 |
| 900 | 23.9 | 14.4 | 0.5 | 0.1 | – | 61.1 |

Following annealing at 900 °C, the titanium content of the near-surface layers was determined to be 23.9 at. % The aluminium content in the near-surface layers was 14.4 at. %, representing a

2.4-fold increase compared to the aluminium content after annealing at 700 °C. This is attributed to the flaking of a portion of the oxide film that occurred during annealing at 900 °C.

The partial flaking of the oxide film can be attributed to the reduction in adhesion of oxide layers to the metal substrate with increasing layer thickness [2]. Additionally, the flaking of the oxide film may also be attributed to the elevated oxidation rate [3]. Moreover, the disturbance of the equilibrium between tensile stresses in the suboxide alpha-layers and compressive stresses in the oxide layers may also contribute to the partial flaking of the oxide film. This is because the prolongation of the oxidation time of the alloy at a given temperature is accompanied by an increase in the residual stress values in the diffusion layer [4].

The data obtained following one-hour annealing at 900 °C demonstrate an elevated aluminium content and a diminished titanium content in the near-surface layers of the TC25 alloy, indicating a proclivity for a reduction in aluminium concentration in the oxide film as one progresses away from the metal-oxide film interface. The obtained data on aluminium distribution are in agreement with the results of previous studies, namely [5], which demonstrated the enrichment of aluminium in the inner layers of the oxide film at the alloy interface, and [4], which showed that as the metal-oxide film interface is approached, the aluminium content in the alloy gradually increases and the titanium content decreases.

### *3.2. X-ray diffraction analysis*

According to the phase composition of sample in Fig. 1, obtained using XRD, the main phase of the initial sample is a solid solution of aluminum in a GPU α-Ti lattice.

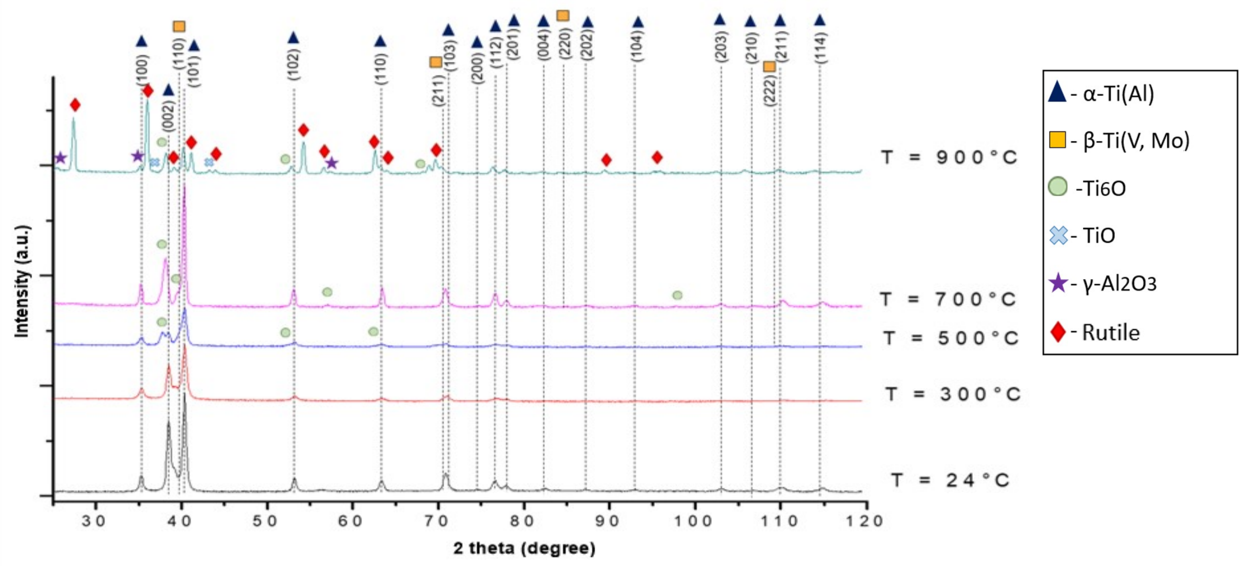

Fig. 1. XRD-spectra of the TC25 alloy before oxidation and after annealing at temperature *T* for one hour in air.

At a temperature of 300 °C, the alloy exhibits good oxidation resistance. After annealing at 500 and 700 °C, the oxygen content in the near-surface layers increased to 42 at. %, which led to the formation of an additional $Ti_6O$ oxide phase. After heat treatment at 900 °C, the aluminum content increased to 14 at. %, which indicates the formation of aluminum oxides $Al_2O_3$. The transformation of $Ti_6O$ into $TiO_2$ oxide of rutile modification with a tetragonal crystal structure and the detachment of the oxide layer from the material is observed. The cause of the destruction may be compressive stresses resulting from a significant difference in the volumes of the oxide and metal. An increase in the intensity of the β-phase β-Ti(V, Mo), especially noticeable after 900 °C, may be associated with polymorphic (α+β) → β by transformation.

### *3.3. Microhardness measurements*

Fig. 2 presents the outcomes of microhardness *H* measurements of the TC25 alloy in its initial state and following one-hour annealing at $T = \{300, 500, 700\}$ °C. Following annealing at 900 °C, microhardness measurements were not conducted due to the partial flaking of the oxide film, which resulted in a significant increase in measurement error and rendered the results unreliable.

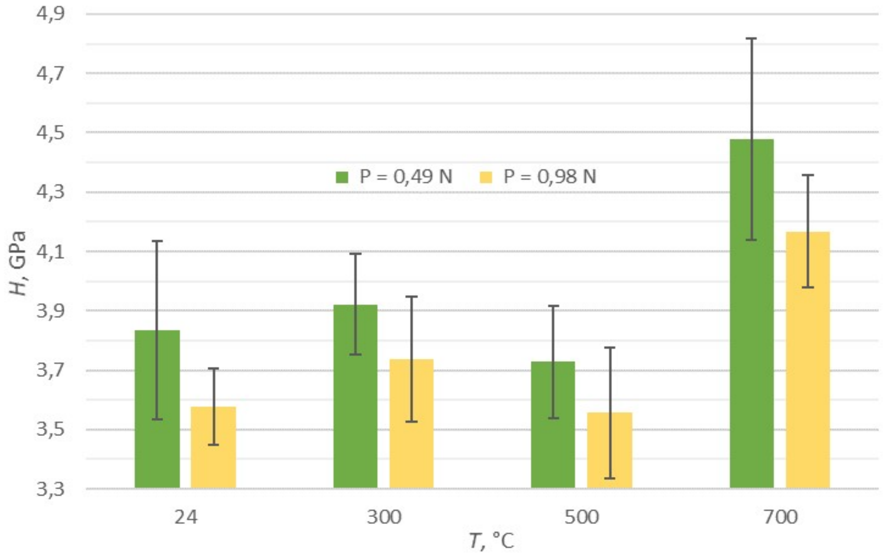

Fig. 2. Dependence of microhardness *H* of the TC25 alloy on annealing temperature *T* for one hour in air, $P = \{0.49, 0.98\}$ N.

The microhardness values of the TC25 alloy in the initial state were 3.8 GPa and 3.6 GPa for the corresponding loads $P = \{0.49, 0.98\}$ N. Following one-hour annealing at 300 °C and 500 °C, the microhardness value remained unchanged, indicating that the thickness of oxide films is relatively small. Following an hour of annealing at 700 °C, the microhardness value of the TC25 alloy increased by 18% in comparison with the initial state. This increase in microhardness is in accordance with the findings of [3, 6, 7] and can be attributed to the formation of a solid oxide layer and deformations resulting from the dissolution of oxygen in the substrate metal [3].

### *3.4. Friction coefficient measurements*

Fig. 3 illustrates the dependence of the friction coefficients of the TC25 alloy on the distance in the initial state and following one-hour annealing treatments at temperatures of $T = \{300, 500, 700, 900\}$ °C.

The mean value of the friction coefficient for the TC25 alloy in its initial state was determined to be 0.55. The same average values of friction coefficients were obtained following one-hour annealing at 300 °C and 500 °C, which indicates the stability of the tribological properties of the TC25 alloy up to 500 °C. Following an hour of annealing at 700 °C, the coefficient of friction exhibited a notable decline, averaging 0.15. Additionally, it demonstrated enhanced stability compared to the preceding states of the TC25 alloy. This result is consistent with the data presented in [8], which demonstrated a decrease in the $E : H$ ratio (*E* is Young's modulus), or plasticity coefficient, which is proportional to the aforementioned ratio. In the same study, it was demonstrated that following the oxidation treatment of the titanium-aluminium alloy, not only did the $E : H$ ratio decrease, but also the elastic recovery increase, resulting in a high elastic contact coefficient. This, in turn, leads to a low adhesion between the contacting surfaces of the counterbody and the alloy, and consequently, to a low and stable coefficient of friction. However, after an hour of annealing at 900 °C, the coefficient of friction increased to an average of 0.30, indicating a decline in stability compared to the previous state of the TC25 alloy.

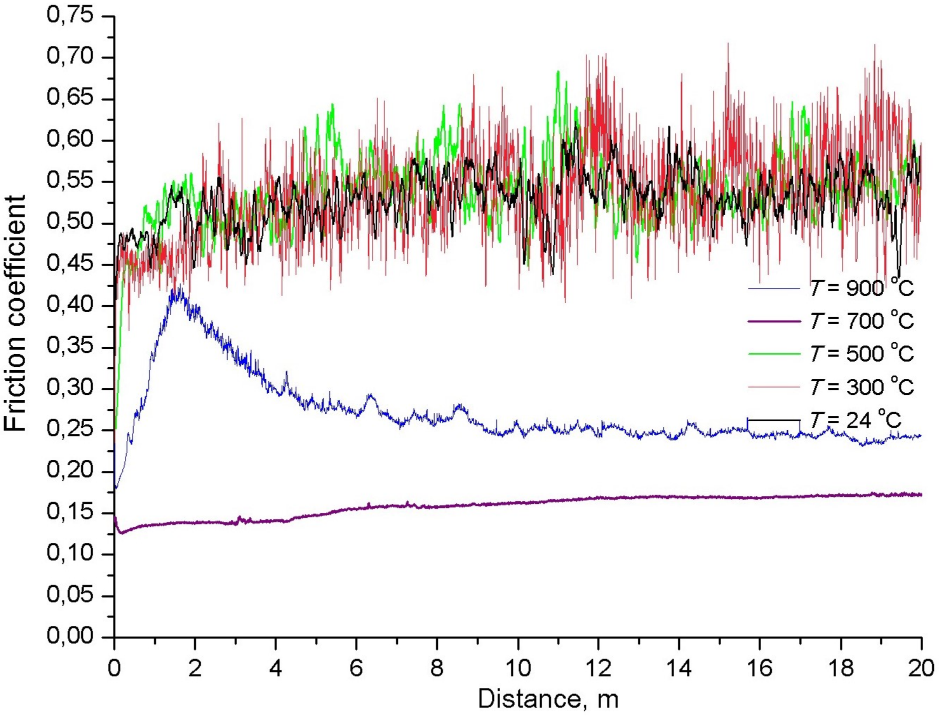

Fig. 3. Dependence of friction coefficient of the TC25 alloy on distance for $T = \{24, 300, 500, 700, 900\}$ °C, $P = 0.49$ N.

### *3.5. Wear resistance*

Table 2 illustrates the quantitative alteration in wear track area *PS*, profile width *PW* and profile height *PH* of the tracks resulting from the measurement of the friction coefficient in the initial state and subsequent to one-hour annealing at temperatures of 300 °C and 500 °C.

**Table 2.** Wear track area *PS*, profile width *PW* and profile height *PH* of the tracks of the TC25 alloy track in the initial state and after one-hour annealings at 300 °C and 500 °C.

| $T$, °C | $PS \cdot 10^{-2}$, μm$^2$ | $PW$, mm | $PH$, μm |
|---|---|---|---|
| 24 | 14.4 ± 2.4 | 0.17 ± 0.01 | 6.6 ± 0.9 |
| 300 | 12.9 ± 2.2 | 0.17 ± 0.01 | 6.1 ± 0.8 |
| 500 | 9.8 ± 2.0 | 0.15 ± 0.01 | 5.0 ± 0.7 |

The data for the TC25 alloy state corresponding to one-hour annealing at 700 °C are not provided, as this track was not recorded by the profilometer. This indicates that the values of the geometrical parameters of the track are comparable to the surface roughness.

As illustrated in Table 2, the track parameters exhibit a decline with elevated annealing temperatures. This phenomenon directly correlates with the enhancement of the alloy's wear resistance, which is observed up to 700 °C. This outcome is consistent with the findings of previous studies, as [3, 6, 7, 9]. The wear track developed on the untreated alloy comprised rough shear deformation features aligned to the direction of sliding, and untreated surface was steadily worn off by shear delamination and smearing [9]. The oxide film prevented the wear of the titanium-aluminium alloy for a certain test time [9]. Thus, it follows from the tribological analysis that the formation of an oxide layer counteracts the reduction of area or limits the loss of material during abrasive wear.

### *3.6. Oxidation scheme*

Based on the works [4, 10] and our own experimental data, we proposed the following scheme for the formation of oxide films on titanium-aluminum alloys (Fig. 4).

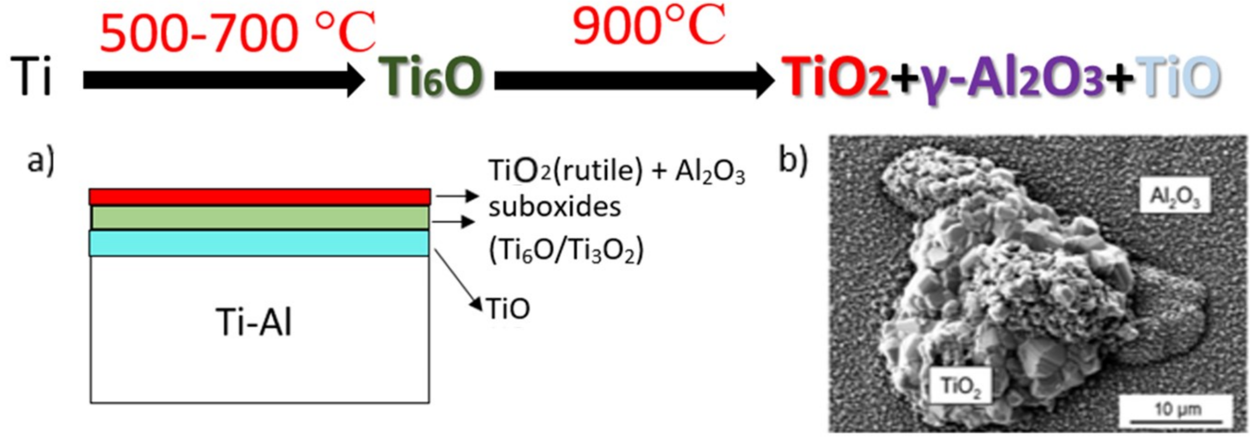

Fig. 4. a) Schematic representation of the formation of a multilayer oxide film on the Ti–Al alloy during oxidation at 900 °C; b) The surface of the γ-TiAl alloy after exposure at high temperatures [11].

In the temperature range up to 700 °C, a stable suboxide layer of $Ti_6O$ or $Ti_3O$ is formed. When the oxygen content exceeds 50 at. %, the formation of TiO and $TiO_2$ occurs. $Al_2O_3$ is predominantly situated within the interior of the oxide film, comprising discrete grains within the volume occupied by rutile. As we approach the metal–oxide film interface, there is an increase in the aluminium content of the alloy and a corresponding decrease in the titanium content. Following an hour-long annealing period at 700 °C, the formation of an oxide film comprising the $Ti_6O$ phase was observed. This finding indicates that this temperature is the optimal annealing temperature for improving the mechanical and tribological properties of the TC25 alloy. At 900 °C, the oxide film exhibited partial flaking, indicating a disruption in the equilibrium between tensile stresses in the alpha-oxide layers and compressive stresses in the oxide layers.

## 4. Conclusion

The objective of this study was to examine the impact of heat treatment in an air environment at elevated temperatures on the mechanical and tribological properties of titanium-aluminium alloys. The results of the conducted experiments permit the following main conclusions to be drawn:

– The TC25 alloy is resistant to oxidation at 300 °C. At temperatures exceeding 500 °C, an oxide film forms on the surface of the alloy, which affects its mechanical and tribological properties, particularly after one hour of annealing at 700 °C.

– The optimal annealing temperature for enhancing the mechanical and tribological properties of the TC25 alloy is 700 °C. This is evidenced by the fact that after one hour of annealing at 700 °C, the alloy exhibited the most favourable mechanical and tribological properties in comparison with other states of this alloy, with an increase of 0.7 GPa (18%) in microhardness at $P = 0.49$ N, a 3.7-fold decrease in the coefficient of friction at $P = 0.49$ N, and a significant improvement in the profile height and wear track area, which decreased by an average of 1.3 and 1.5 times, respectively, compared to the initial state.

– After one hour of annealing at 900 °C, the oxide film showed partial delamination from the surface of the TC25 alloy, indicating that further increases in annealing temperature may not be useful in improving the mechanical and tribological properties. A more detailed investigation of the changes in the mechanical and tribological properties of the TC25 alloy after annealing at 700 °C and close to it, with different annealing times, would be beneficial.

## 5. References

[1] D. Wu, et al., New high-strength Ti–Al–V–Mo alloy: from high-throughput composition design to mechanical properties, International Journal of Minerals, *Metallurgy and Materials*, vol. **26**, 1151–1165, 2019, doi: 10.1007/s12613-019-1854-1

[2] C. Coddet, A.M. Craze, G. Beranger, Measurements of the adhesion of thermal oxide films: application to the oxidation of titanium, *Journal of Materials Science*, vol. **22**, 2969–2974, 1987, doi: 10.1007/BF01086499

[3] H. Guleryuz, H. Cimenoglu, Surface modification of a Ti–6Al–4V alloy by thermal oxidation, Surface and Coatings Technology, vol. **192**, 164–170, 2005, doi: 10.1016/j.surfcoat.2004.05.018

[4] Lazarev E.M., Kornilova Z.I., Fedorchuk N.M., *Okslenie titanovykh splavov (in Russian)*. Moskva: Nauka, 1985.

[5] A.V. Revyakin, *Titan i ego splavy (in Russian)*. Moskva: AN SSSR, 1962.

[6] K. Aniolek, et al., Mechanical and tribological properties of oxide layers obtained on titanium in the thermal oxidation process, *Applied Surface Science*, vol. **357**, 1419–1426, 2015, doi: 10.1016/j.apsusc.2015.09.245

[7] A. Kumar, et al., Evaluation of mechanical properties of titanium alloy after thermal oxidation process, *Transactions of the Indian Institute of Metals*, vol. **73**, 1373–1381, 2020, doi: 10.1007/s12666-020-01978-w

[8] H. Dong, et al., Surface engineering to improve tribological performance of Ti–6Al–4V, *Surface engineering*, vol. **13**, 402–406, 1997, doi: 10.1179/sur.1997.13.5.402

[9] H. Guleryuz, H. Çimenoglu, Effect of thermal oxidation on corrosion and corrosion–wear behaviour of a Ti–6Al–4V alloy, *Biomaterials*, vol. **25**, 3325–3333, 2004, doi: 10.1016/j.surfcoat.2004.05.018

[10] K.L. Luthra, Stability of protective oxide films on Ti-base alloys, *Oxidation of metals*, vol. **36**, 475–490, 1991, doi: 10.1007/BF01151593

[11] C. Leyens, et al., Recent progress in the coating protection of gamma titanium-aluminides, *JOM*, vol. **58,** 17–21, 2006, doi: 10.1007/s11837-006-0062-4