Rafidain Journal of Science

https://rsci.uomosul.edu.iq

Vol. 34, No. 3, pp. 102-112, 2025 (September)

Study of the Efficiency of Single Annealing of Pure Titanium and Titanium Alloy in Resisting Cyclic Oxidation at 900°C

Khalid Sh. Mahmoud
Department of Physics/ College of Education for Pure Applied Science/ University of Tikrit/ Tikrit
Zuheer N. Majeed
Department of Physics/ College of Education for Girls/ University of Kirkuk/ Kirkuk
Mahmoud A. Hammond
Department of Physics/ College of Science/ University of Mosul/ Mosul

p-ISSN: 1608-9391
e -ISSN: 2664-2786

Article information

Received: 9/2/2025
Revised: 14/4/2025
Accepted: 24/4/2025

DOI: 10.33899/rjs.2025.189222

corresponding author:
Khalid Sh. Mahmoud
ah230073ued@st.tu.edu.iq
Zuheer N. Majeed
zuheernaji@uokikuk.edu.iq
Mahmoud A. Hammond
dr.mhmood@uomosul.edu.iq

ABSTRACT

The purpose of the research is to modify the surface of pure titanium and titanium alloy using a single aluminized coating system (cementation) at 1000^{o}C, which led to structural changes in the surface of the aluminized models and to study the efficiency of this coating in resisting oxidation through a periodic oxidation test at a temperature of 1000^{o}C for 150 hours. Microscopic examinations were conducted with a scanning electron microscope (SEM-EDS) and X-rays on the aluminized samples to determine the structures and phases that formed as a result of aluminization, which had a major role in improving the resistance of pure aluminized titanium and titanium alloy to oxidation and corrosion compared to the non-aluminized models, as the efficiency of the coating on the titanium alloy was better than its efficiency on pure titanium, and the reason is due to the formation of a thin protective layer of alumina with high adhesion and high thermal stability.

Keywords: Diffusion coating, special aluminum coating, hot corrosion, cementation, pure aluminum alloy.

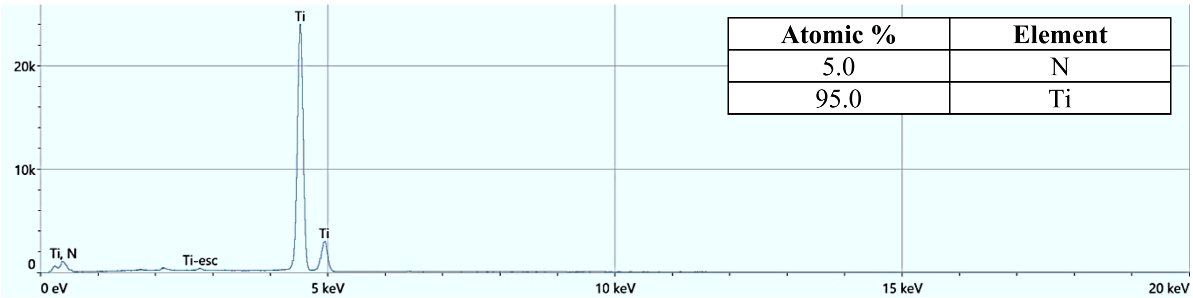
INTRODUCTION

Ti alloys been put to use for various structural purposes because of their great strength, light weight, temperature durability, excellent corrosion resistance, ability to withstand extreme temperatures, and good physical and mechanical specifications characterized by low density and high specific strength (Aimi *et al.*, 2004; Hao *et al.*, 2007; Dai *et al.*, 2016; Tarselli., 2013). There is a great and expensive difficulty to reduce the permeability of oxide into titanium metal (Flower, 2000; Chen *et al.*, 2000). Among the techniques of safeguarding metals from corrosion and oxidation is the diffusion coating or the so-called ordinary (Pack Cementation) (Xiang *et al.*, 2003a; Gurrappa, 2001; Koo and Yu, 2000), which is known for its effectiveness in protecting metals from oxidation and corrosion as well as its low cost. By creating a casing of aluminum oxide (alumina) type alpha, which is known for its high thermal stability and high resistance to harsh environmental conditions, so that these alloys are safe to use, even when operational temperatures are comparatively high. Periodic studies on isothermal oxidation at (800°C) revealed that the alumina coating the simple resulting from aluminum filling shows superior resistance to oxidation in comparison to uncoated alloys. Considering the outcomes through various methods, simple aluminum coating is an economical, simple and effective coating to prevent corrosion of the metal through the creation of a coating of aluminum oxide that envelops the model and prevents its interaction with the external environment, thus providing excellent protection and preventing oxidation of the components from which the alloy is made (Clarke and Phillpot, 2005; Barbezat, 2006; Bose, 2007; Parlak and Ayhan, 2007; Yang *et al.,* 2024).

The formation of a thin layer of TiO_2, which is formed spontaneously when the surface of the clean metal is exposed to air (Ahmed, 2023), is resistant to oxidation. However, at temperatures above (600°C), this ant oxidation property is significantly lost by the metal (Yilmaz, 2010). Because of this effect the use of titanium alloys is prohibited in high temperature environments, for example in gas turbines, as well as the maximum application temperature of Ti-6Al-4V alloy is less than (350ºC) due to its poor resistance to oxidation at high temperatures (Li *et al.*, 2012). Titanium alloy Ti-6Al-4V cannot therefore be used to produce propeller blades and first and second blades for aircraft engines (Bose, 2007). When temperatures are high, oxygen enters the underground region of (Ti alloy) and (Ti) aluminized, which leads to a few negative consequences. Therefore, it is well suited for it if large experimental efforts are made to increase the resistance to oxidation of titanium alloys (Ti) at elevated temperatures in distinct ways and methods, including the addition of a layer of aluminum mediated by the diffuse coating process of aluminum or what is known as (Almena) at the surface of sample. Single alumina coatings are one of the most promising coatings for advanced gas turbines (Flower, 2000), but they still face challenges related to higher temperature tolerance, longer service life, and higher reliability. In high-temperature service, due to the thermal stress mismatch between the alloy coating and the oxide film, the peeling of the oxide film from the alloy substrate is the root cause of coating failure. However, thermal barrier coatings and the use of active Y or rare earth elements as barriers in the alloy can significantly enhance the adhesion between the alloy and the oxide film (Chen *et al.*, 2000; Xiang, 2003b). This significantly improves the oxidation resistance at high temperatures and extends the alloy's operational life and service life. This is due to the formation of complex oxides such as Y-Al-O_3 (yttrium aluminum perovskite) and phase changes that increase oxidation resistance and prevent cracking, which is the main cause of failure and collapse.

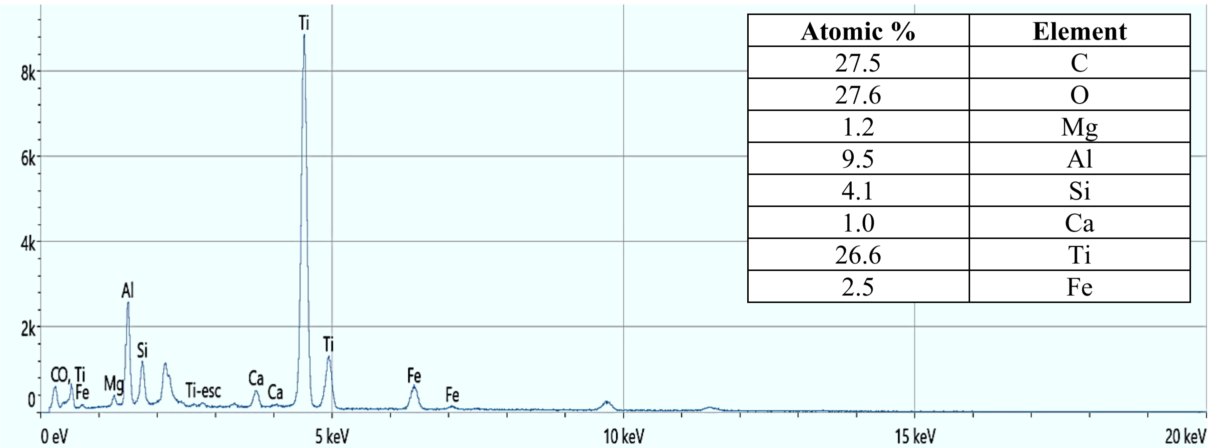
EXPERIMENTAL PROCEDURE

Samples of pure titanium and titanium alloy detailed in Fig. (1) and Fig. (2) obtained through energy dispersion spectrometry (EDS) were used.



Atomic %	Element
5.0	N
95.0	Ti

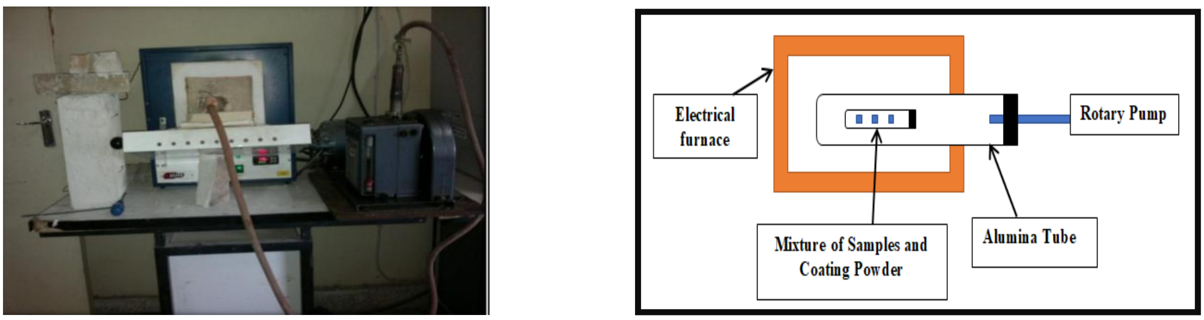
Fig. 1: Energy dispersion spectrogram (EDS) for a pure titanium slice.



Atomic %	Element
27.5	C
27.6	O
1.2	Mg
9.5	Al
4.1	Si
1.0	Ca
26.6	Ti
2.5	Fe

Fig. 2: Energy dispersion spectrogram (EDS) for titanium alloy slice.

Single-aluminized aluminum coating methods were applied. A mixture of the coating element, which is aluminum (30%) as the coating material, aluminum oxide (alumina) (66%) as the material that helps avoid the agglomeration of the mixture, and ammonium chloride powder was used to perform the unique manization process of all generated samples. Using 4% as a stimulant, the mixture is progressively poured into the capsule while the samples to be painted are applied. As illustrated in Fig. (3a, b), the capsule is sealed and put within a vacuum oven. After the painting process is finished, the samples are removed immediately and allowed to cool and clean for a while. They are then weighed, the difference between their pre- and post- Germanization weights is calculated, and the net weight is divided by the sample area to determine the weight gained per unit area. The oven temperature is set to the necessary level (1000°C) for four hours.

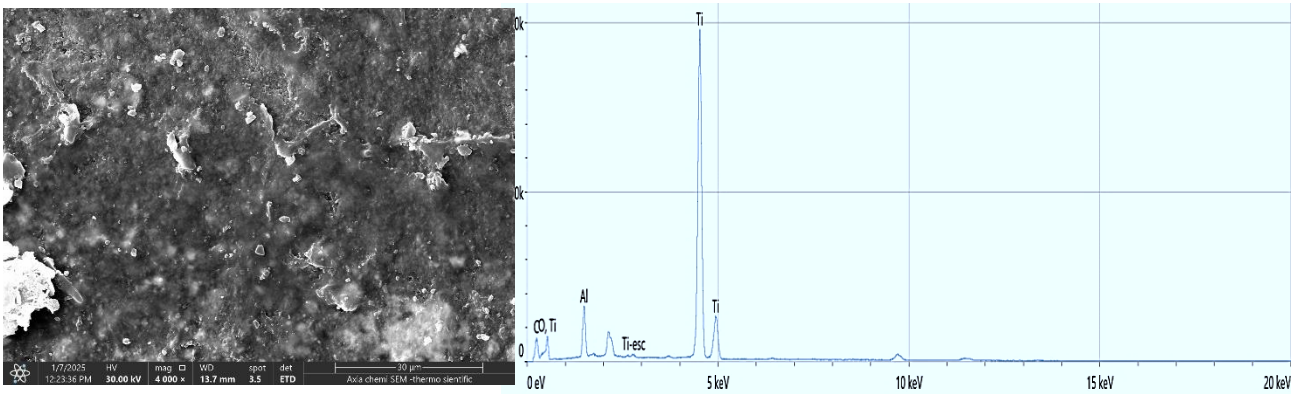


(a) **(b)**

Fig. 3: (a) Illustrative image showing the paint system. (b) Diagram of the paint system.

RESULTS AND DISCUSSION

The results of the analyses (SEM-EDS-XRD (Xpert High Score Plus)) mentioned in (Tables 1, 2, 3 and 4) and in Fig. (4a, b), Fig. (5a, b), Fig. (6a, b), Fig. (7a, b), Fig. (8a, b) and Fig. (9a, b) confirm that the process of single aluminum coating at 1000°C and in a vacuum atmosphere (10^{-3}-10^{-2} torr) within four hours has resulted in the enrichment of the alloy's surface with the paint element, which is aluminum. This is further supported by the surface images of the models taken with optical microscopy following polishing and refinement operations for the models under study and using the demonstration solution, which shows the composition of the coating layers and their thickness. The two slides exhibit some morphological similarity due to this covering.



(a) (b)

Fig. 4: (a) Pure titanium chip components. (b) Quantitative and qualitative spectroscopy analysis of pure aluminum coated titanium chip at (1000°C) temperature for (4 hours).

(a)
(b)

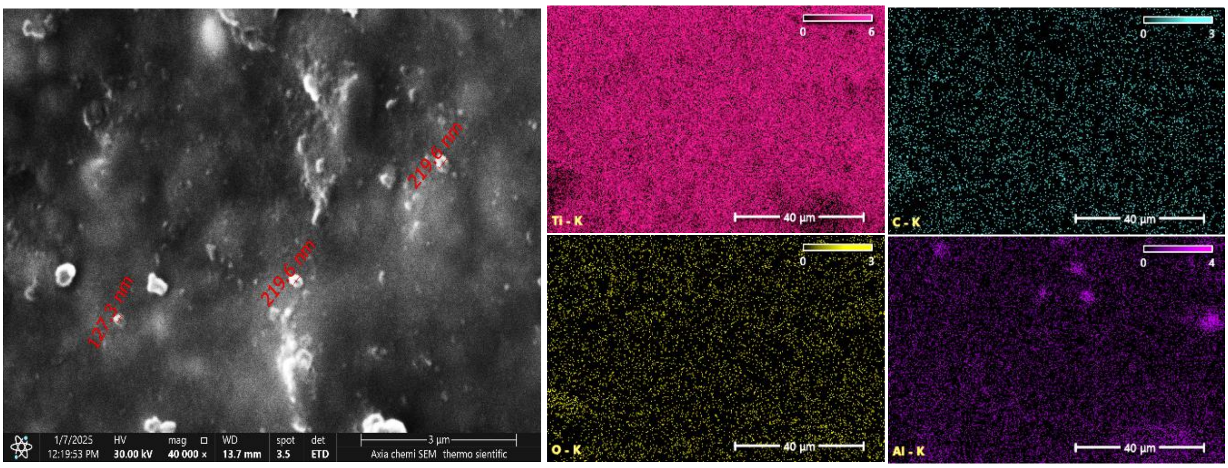
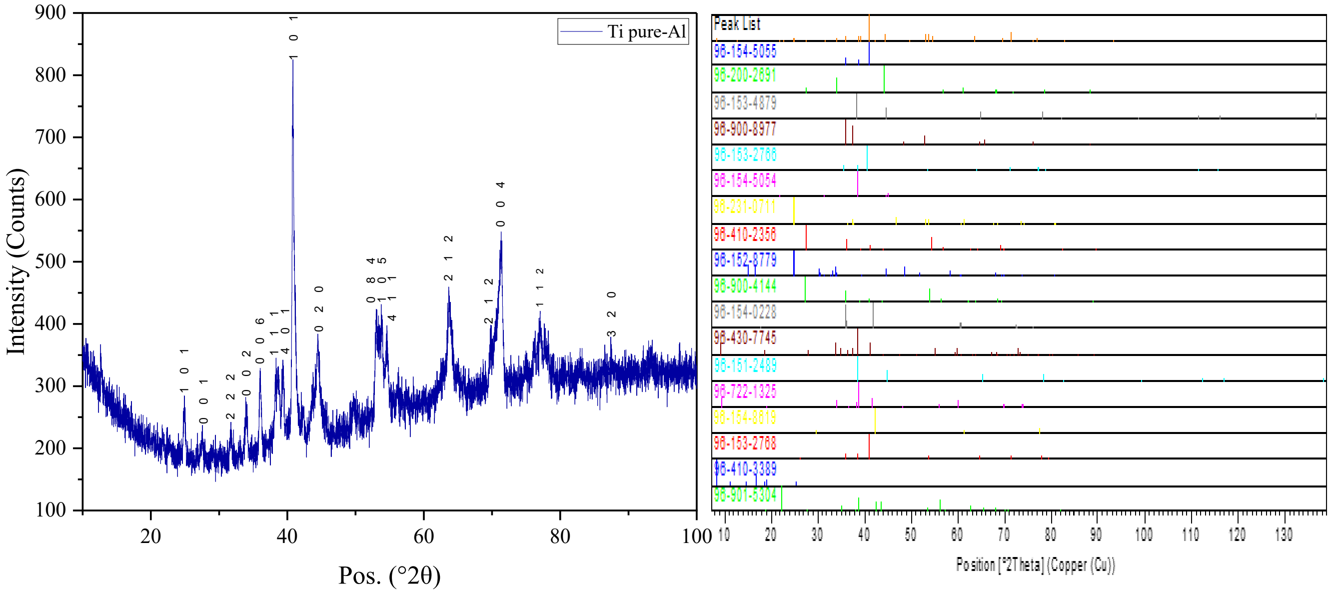


Fig. 5: (a) Surface composition of pure titanium alloy coating aluminized by single aluminization time 4h. (b) Concentrations and distribution of elements shown in the (EDS) test.

Table 1: Weighing ratios using the SEM-EDS electron scanner for the pure titanium strip at 1000°C for 6 hours.

Element	Single Aluminization - Wt%
C	27.4
O	36.2
Al	6.4
Ti	30.0
Total	**100.00**

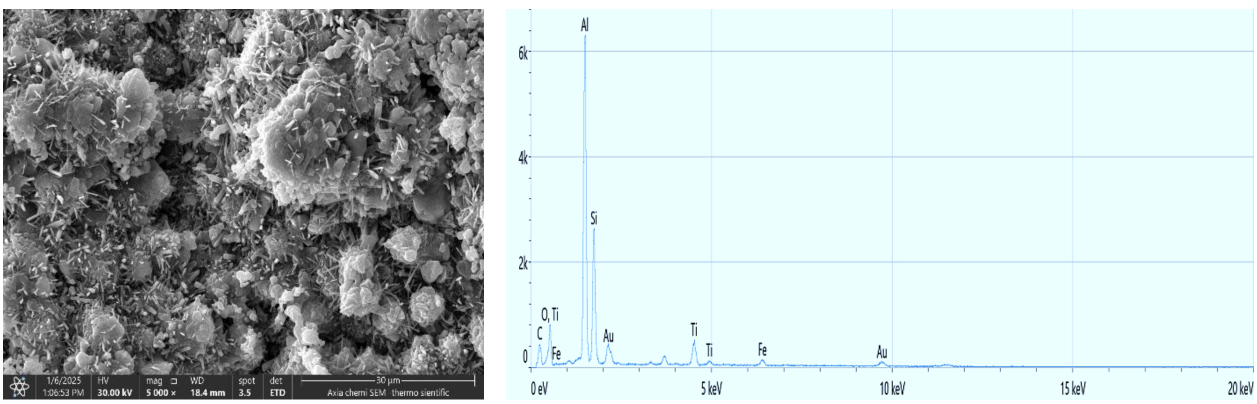


(a) (b)

Fig. 6: (a) XRD diagram of pure titanium alloy anodized by single aluminization-time (4h). **(b) XRD spectral lines of pure titanium single alumina alloy-time (4h).**

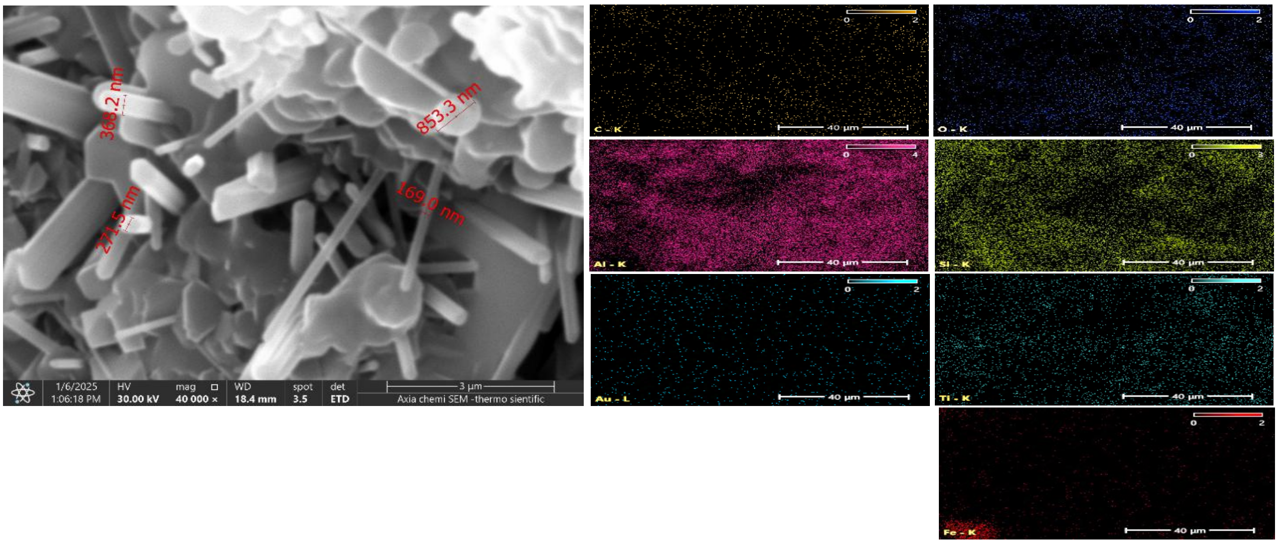
Table 2: Some expected phases extracted from X-ray diffraction (XRD) examination of the single aluminized pure titanium alloy, time (4h).

Ref. code	Compound name	Chemical formula
96-154-5055	Aluminum Titanium	AlTi
96-200-2691	Titanium (II) oxide - HT	TiO_2
96-153-4879	Titanium	Ti_4
96-153-2766	Titanium	Ti_2
96-231-0711	Titanium (II) oxide	TiO_2
96-722-1325	Aluminum Titanium Carbide	$Ti_3 Al C_2$
96-410-3389	Aluminum Oxide Carbon	C_3AlO_5
96-901-5304	Aluminum Oxide	Al_2O_3



(a) (b)

Fig. 7: (a) Titanium alloy sample components. **(b) Quantitative and qualitative spectroscopy analysis of aluminum coated titanium alloy slice at 1000°C for 4 hours.**

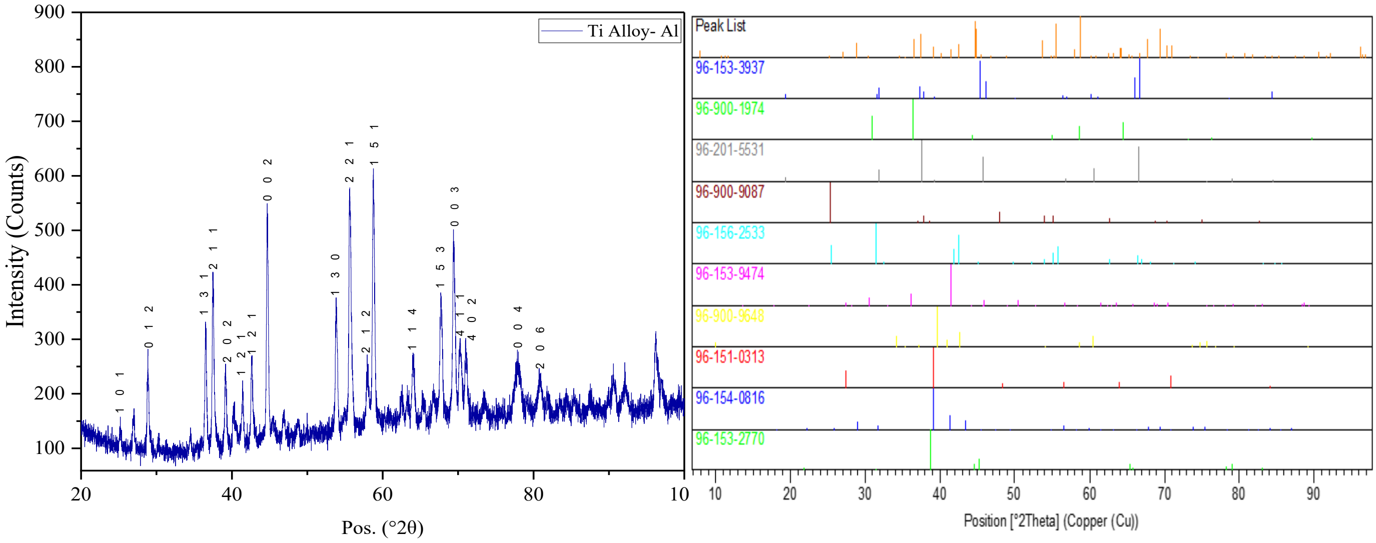


(a) (b)

Fig. 8: (a) Surface composition of titanium alloy coating aluminized by single aluminization time 4h. (b) Concentrations and distribution of elements shown in the (EDS) test.

Table 3: Weighing ratios using the electronic scanner (SEM-EDS) for the coating (single with aluminum) of the titanium alloy slice at 1000°C for 6 hours.

Element	Single Alumimization - Wt%
C	23.4
O	21.3
Al	27.1
Si	16.5
Ti	4.2
Fe	1.3
Au	6.2
Total:	**100.00**



(a) (b)

Fig. 9: (a) XRD diagram of titanium alloy anodized by single aluminization-time 4. (b) XRD spectral lines of titanium single alumina alloy-time 4h.

Table 4: Some expected phases extracted from X-ray diffraction (XRD) examination of the single aluminized titanium alloy, time 4h.

Ref. code	Compound name	Chemical formula
96-153-3937	Aluminum Oxide	Al_2O_3
96-900-1974	Hercynite	$FeAl_2O_4$
96-201-5531	Aluminum Oxide	Al_2O_3
96-900-9087	Anatase	TiO_2
96-156-2533	Titanium Dioxide - II	TiO_2
96-151-0313	Titanium Gold	AuTi
96-154-0816	Aluminium Gold	Au_4Al
96-153-2770	Titanium Aluminium	Ti Al

After the surface polishing processes were completed, the coated samples were examined under a microscope with varying magnification powers. The coating structure was determined by etching with a nital solution, which is composed of distilled water, hydrofluoric acid (HF), hydrochloric acid (HCl), and nitric acid (HNO_3). As shown in Fig. (10a, b), microscopic analysis revealed that the area affected by the aluminum coating process consists of two layers: The outer layer and the inner diffusion layer and this is what SEM images with a magnification power of 1mm revealed.

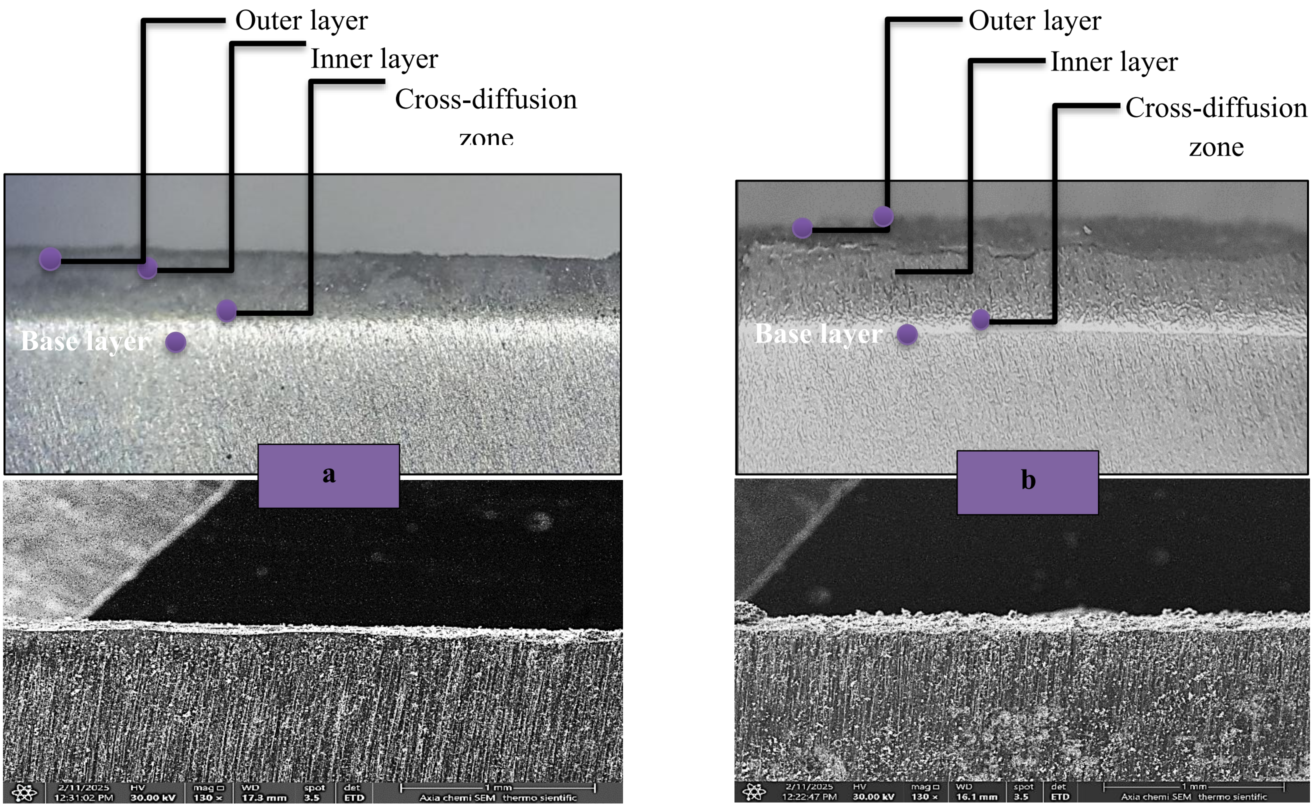
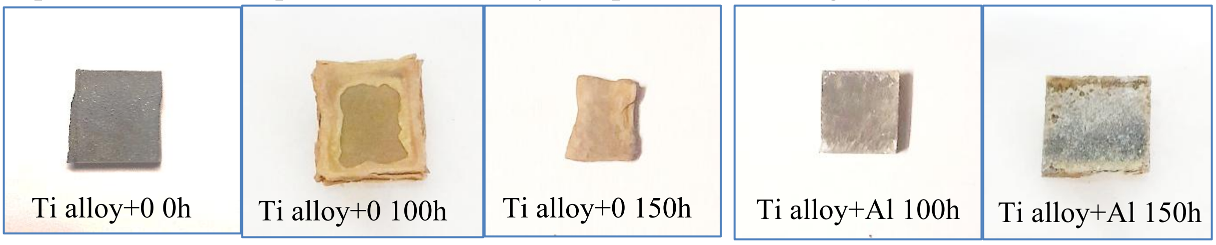


Fig. 10: Microstructure and (SEM) images of pure titanium slat and aluminum-coated titanium alloy chip: (a) Pure titanium chip. (b) Titanium Alloy chip. At a temperature of 1000°C for 4 hours.

The thermal periodic oxidation method was used to study the kinetics of oxidation and hot corrosion. The samples are placed in an electric furnace set at 900°C, and after 5 hours of oxidation, they are removed from the furnace and allowed to cool to room temperature. Following each cycle, samples are weighed to ascertain the weight change and then put back in the oven. For 150 hours, this procedure is conducted on a periodic basis. The sample photos Fig. (11a, b) demonstrate that the painful titanium alloy samples demonstrated resistance to oxidation and heat corrosion in comparison to the non-painful titanium alloy sample, as seen in Fig. (12).



(a) (b)

Fig. 11: Surface appearance of two samples of non-painful titanium alloy (a) and (b) painful both at 900°C for 100h and 150h.

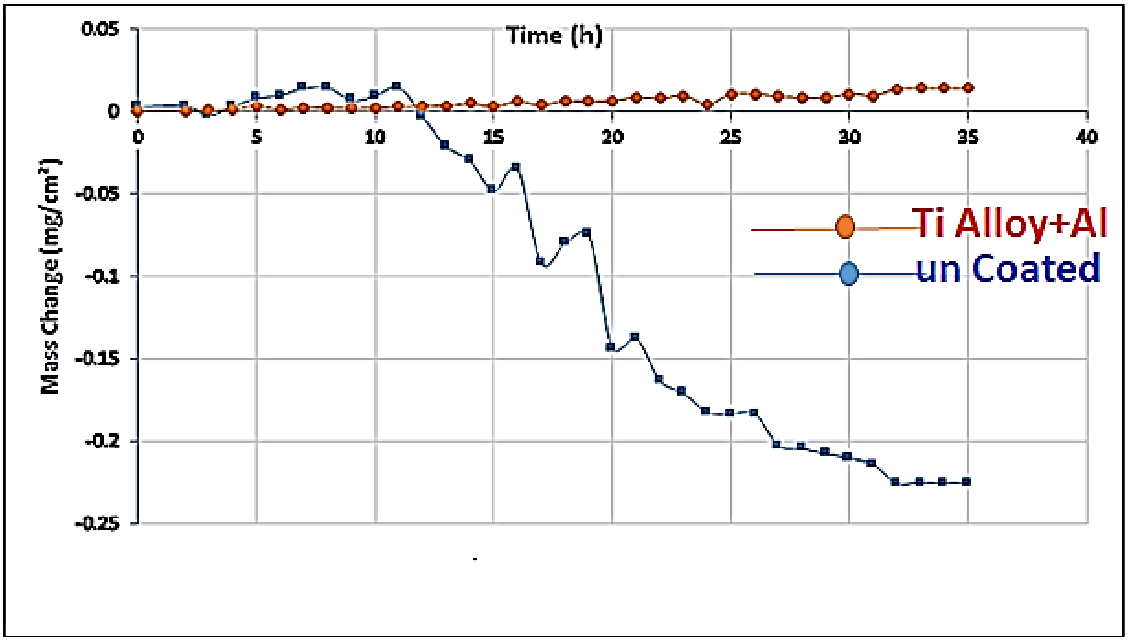
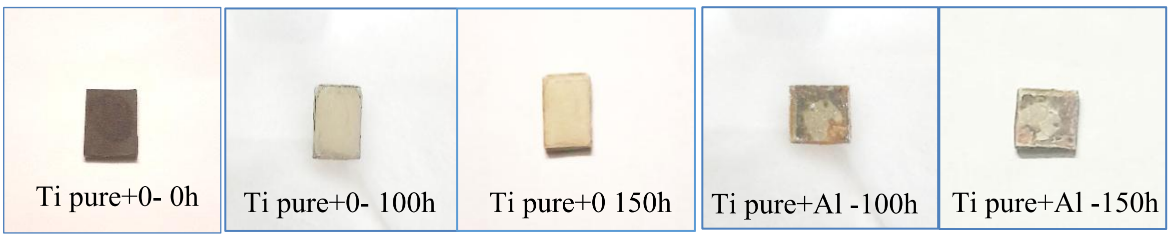


Fig. 12: Hot corrosion, non-painful titanium alloy sample and titanium alloy sample at 900°C for 150 hours.

The structural structure that results from analysis and the coating layers that form on the surfaces of the painful samples as opposed to the non-painful and exposed to oxidation and thermal corrosion as in Fig. (13) demonstrate the improvement in the oxidation resistance and hot corrosion of the pure titanium metal samples (Ti Pure) in comparison to the non-painless titanium samples Fig. 14(a, b).



(a) (b)

Fig. 13: Surface appearance of pure titanium. (a) Non-metallic. (b) Painful strips at 900°C for 100h and 150h.

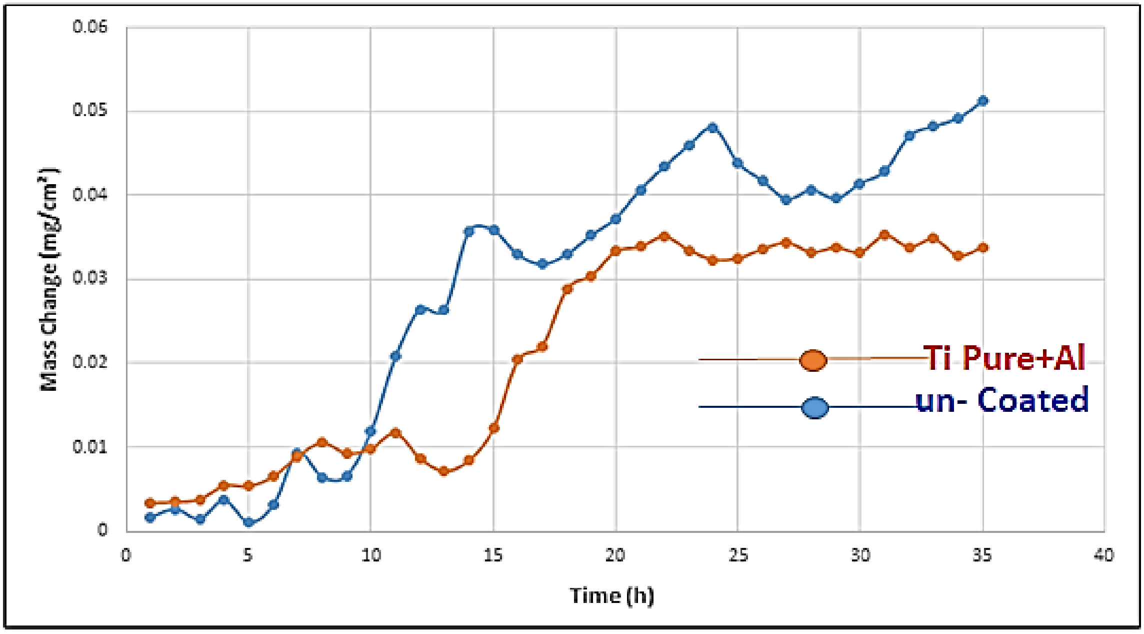


Fig. 14: Hot corrosion of pure non-metallic titanium samples and painful pure titanium samples at a temperature of 900ºC for 150 hours.

CONCLUSIONS

By testing the coatings used in this study on samples of pure titanium and titanium alloys, it was shown that the aluminized titanium alloys were highly effective in resisting cyclic oxidation and preventing corrosion due to the formation of a protective and thermally stable layer of aluminum oxide. Furthermore, various phases of aluminum were formed with titanium and other elements present in the titanium alloy, which have good properties in protecting the metal from harsh environmental conditions. Therefore, no changes in size, color, or shape were observed in the alloy. These phases formed as a result of phase changes resulting from heat treatment during cyclic oxidation, a finding supported by XRD (SEM-EDS) data. Unlike the corrosion-resistant titanium alloy chips, which contain thick layers of alloying oxides instead of aluminum, causing corrosion after peeling off the oxide layer during cyclic oxidation for 150 hours at 900°C, the formation of thin layers of aluminum oxide (Al_2O_3) isolated the samples from their surroundings and provided superior protection against oxidation and thermal corrosion. Pure titanium (Ti Pure) samples coated with aluminum exhibited good corrosion protection and the ability to form well-adhered (TiO_2) layers under the same conditions, resulting in increased sample mass. The good protection and stable mass of the sample are attributed to the production of aluminum oxide (Al_2O_3) in the inner layer and titanium dioxide (TiO_2) in the outer layer.

ACKNOWLEDGMENTS

I would like to express my deepest gratitude to the College of Science, Department of Physics, University of Mosul, for providing me with the opportunity to conduct this research. I would like to extend my special thanks to my supervisors, colleagues, and friends, who have supported me throughout this research.

REFERENCES

Ahmed, M. (2023). The effectiveness of TiO_2 thermal barrier coating in protecting IN738 LC super alloy in an atmosphere of sodium sulfate and sodium chloride vapor at high temperature. *Inter. Acad. J. Sci. Eng.*, **10**(1), 20-26. DOI:10.9756/IAJSE/V10I1/IAJSE1004

Aimi, M.F.; Rao, M.P.; Zuruzi, A.S.; Bothman, D.P. (2004). High-aspect-ratio bulk micromachining of titanium. *Nat. Mat.*, **3**(2), 103-105. DOI:10.1038/nmat1058

Barbezat, G. (2006). Application of thermal spraying in the automobile industry. *Surf. Coat. Tech.*, **201**(3-4), 2028-2031. DOI:10.1016/j.surfcoat.2006.01.027

Bose, S. (2007). High-temperature coatings. *App. Therm. Eng.*, **9**(1), 150-155. DOI:10.1016/j.applthermaleng.2005.01.015

Chen, G.Z.; Fray, D.J.; Farthing, T.W. (2000). Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride. nature, **407**(6802), 361-364. DOI:10.1038/35030069

Dai, J.; Zhu, J.; Chen, C.; Weng, F. (2016). High Nb containing TiAl alloys. *J. All. Comp.*, **685**, 784-798. DOI:10.1016/j.jallcom.2016.06.212

Flower, H.M. (2000). Materials science: A moving oxygen story. *Nat.*, **407**(6802), 305-306. DOI:10.1038/35030266

Gurrappa, I. (2001). Platinum aluminide coatings for oxidation resistance of titanium alloys. *Plat. Met. Rev.*, **45**(3), 124-129. DOI:10.1595/147106701X25611

Hao, Y.; Li, S.; Sun, B.; Sui, M.; Yang, R. (2007). Ductile titanium alloy with low Poisson's ratio. *Phy. Rev. Lett.*, **98**(21), 216405. DOI:10.1103/PhysRevLett.98.216405

Koo, C.H.; Yu, T.H. (2000). Pack cementation coatings on Ti_3Al-Nb alloys to modify the high-temperature oxidation properties. *Surf. Coat. Tech.*, **477**, 130354. DOI:10.1016/j.surfcoat.2019.10.130354

Li, X.; Lu, S.-Q.; Wang, K.-L.; Cao, J.-X.; Huang, X. (2012). High temperature deformation characteristic of as-cast Ti40 burn-resistant titanium alloy. *Cail. Rech. Xue./Trans. Mat. Heat Treat.*, **33**, 28-32.

Parlak, A.; Ayhan, V. (2007). The effects of using a piston with a thermal barrier layer in S.I. engines. *J. Ene. Ins.*, **80**(5), 223-228. DOI:10.1179/174602207X197087

Tarselli, M.A. (2013). Titanium tales. *Nat. Chem.*, **5**. DOI:10.1038/nchem.1656

Clarke, D.R.; Phillpot, S.R. (2005). Thermal barrier coating materials. *Mat. Tod.*, **8**(6), 22-29. DOI:10.1016/S1369-7021(05)70934-2

Xiang, Z.D.; Rose, S.R.; Burnell-Gray, J.S. (2003a). Co-deposition of aluminide and silicide coatings on γ-Ti-Al by pack cementation process. *Journal of Materials Science*, *38*(1), 19–28. DOI:10.1023/A:1021149413017

Xiang, Z.D.; Rose, S.R.; Datta, P.K. (2003b). Codeposition of Al and Si to form oxidation-resistant coatings on γ-TiAl by the pack cementation process. *Mat. Chem. Phy.*, **80**(2), 482-489. DOI:10.1016/S0254-0584(02)00551-5

Yang, Z.; Zhang, J.; Luo, C.; Yu, C.; Li, M.; Han, W. (2024). Effect of pre-oxidation and sea salt on the hot corrosion behavior of MCrAlY coatings and AlSi coatings. *Sur. Coat. Tech.*, **477**, 130354. DOI:10.1016/j.surfcoat.2023.130354

Yilmaz, I.T. (2010). Thermal barrier coatings for diesel engines. *Proc. 10th Inter. Sci. Confer.*, **2**, 173-177.

دراسة كفاءة الالمنة المنفردة للتيتانيوم النقي وسبيكة التيتانيوم في مقاومة الاكسدة الدورية عند 900 درجة مئوية

محمود احمد محمود
جامعة الموصل/ كلية العلوم/ قسم الفيزياء
زهير ناجي مجيد
جامعة كركوك/ كلية التربية للبنات/ قسم الفيزياء
خالد شاكر محمود
قسم الفيزياء/ كلية التربية/ جامعة تكريت

الملخص

ان الهدف من البحث هو التعديل السطحي للتيتانيوم النقي وسبيكة التيتانيوم باستخدام نظام الطلاء الالوميني المنفرد (السمنتة) عند درجة حرارة (1000^oC). والذي ادى الى تغيرات بنيوية في سطح النماذج المؤلمنة ودراسة كفاءة هذا الطلاء في مقاومة الأكسدة من خلال اختبار الاكسدة الدورية عند درجة حرارة 900 درجة مئوية لمدة 150 ساعة أجريت الفحوصات الدقيقة بجهاز الماسح الالكتروني والاشعة السينية على العينات المؤلمنة لمعرفة التراكيب والاطوار التي تشكلت نتيجة الالمنة والتي كان لها دور كبير في تحسين مقاومة التيتانيوم النقي المؤلمن وسبيكة التيتانيوم للأكسدة والتآكل مقارنةً بالنماذج غير المؤلمنة حيث كانت كفاءة الطلاء على سبيكة التيتانيوم افضل من كفاءته على التيتانيوم النقي والسبب يعود لتشكل طبقة رقيقة واقية من الالومينا ذالت الالتصاقية العالية والاستقرارية الحرارية العالية.

الكلمات الدالة: التاكل الحار، السمنتة، الالمنيوم النقي، طلاء الالمنيوم المتفرد، طلاء الانتشار.