Study of the effect of time on the weight gained by the Aluminized method on some ferrous alloys (Steel-H25)

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This research aims to modify the surface components of Steel-H25 alloy by the method of surface engineering through the single diffusion coating technique to obtain new alloys with high efficiency in resisting harsh environmental conditions. Steam a mixture of sodium chloride (NaCl) and sodium sulfate (Na2SO4) at a temperature of 900 C° and then compare it with the base alloy. The results showed that the alloys produced in this way are very efficient. The results showed that the aluminum coating showed high efficiency in resisting oxidation and provided better protection for a longer time compared to the uncoated alloy due to the Al2O3 oxide crust layer formed with high adhesion as well as the aluminum-rich phases, whether the phases were nickel-aluminum or iron-aluminum. The results also showed that the weight gain of the alloy is subject to the parabola relationship with time.

Keywords: Diffusion coating, High-temperature oxidation, Hot corrosion, Parabola relationship, Surface engineering.

1. Introduction

Diffusion coating is one of the most widely used types of coating. It involves several processes, including the interaction or dissolution and diffusion of the coating metal with the substrate. Modifying the surface structure of the metal by diffusion is one of the most common and widely used methods for obtaining the best surface properties (surface alloy). This is because the coating process changes the chemical composition of the surface by diffusion of the coating elements, whether metallic or non-metallic, into the base composition of the alloy. This leads to an alloying process between the base metal and the elements at the surface, which is why it is sometimes called surface alloying.

The surface layer formed after the diffusion coating process is considered part of the base composition. This coating is characterized by the fact that the change in dimensions and composition of the coating is less than the actual surface thickness of the substrate. This change is tolerated in many coating systems. One of its advantages is also the ability to obtain good properties for the coating layer, as the diffusion coating process involves two main operations:

1. Replacing some of the base atoms with the coating material:

This involves preparing the coating material and applying it to the base surface. The coating material can be applied in a variety of ways, such as by spraying, dipping, or electroplating. [1] [2]

2. Diffusion of the coating material into the base metal:

The substrate is heated to a temperature high enough to allow the coating material to diffuse into the surface. The diffusion time and temperature will depend on the coating material, the substrate material, and the desired properties of the coating.

It is worth noting that diffusion coating can be classified into two types:

- Simple Aluminide Coating
- Modified Aluminized Coating:

Pack cementation is a widely used diffusion coating method that offers numerous advantages over other coating techniques. This method is particularly effective in producing coatings that exhibit high resistance to oxidation and hot corrosion at elevated temperatures. Additionally, pack cementation is relatively inexpensive, easy to perform, and compatible with a wide range of metals and advanced alloys (superalloys). The resulting coating is characterized by its uniform composition and thickness, ensuring consistent performance and enhanced material properties[3], This method can be represented through the following steps:

- By immersing the part to be painted in a mixture of the paint metal and the activating substance, which is one of the volatile halides such as (NH_4CI) or (NH_4Br), as it transfers the paint element from the source to the part to be painted.
- Also use a material that prevents the mixture from clumping, such as alumina (Al_2O_3).
- The mixture is then placed in a jar made of alumina and closed tightly.
- It is then placed in an oven that is emptied of air using a vacuum device (Rotary Pump) or by introducing an inert gas such as argon gas (Ar) to prevent oxygen and thus prevent oxidation from occurring.
- The powder is heated to a temperature ranging between (750-11500°C) [4].
- This method played a major role in achieving many different coatings, such as chromizing and siliconizing [5].
- The coatings resulting from this method are affected by many factors, including [6]:

1. Mix ingredients in the powder.
2. Temperature

3. Installation of the foundation alloy.
4. Heat treatment time.

The use of aluminum in the coating process using the Simple Aluminide Coating method is called the pack cementation method, which means aluminization, which can be defined as saturating the surface of the alloy or metal with aluminum (AI) by spreading aluminum atoms into The metal to be coated forms an alloy that is completely different from the composition of the base metal or alloy [7].

- Thermal Barrier Coating (TBCs): Modified Aluminide coating involves the deposition of a secondary layer between the base alloy and the layer obtained by simple aluminum coatings, as the presence of this secondary layer impedes mutual diffusion between the base alloy and the coating layer. The modified aluminum coating also includes the addition of rare earth elements such as (Y, Ce, La) or the oxides of these elements, which work to improve the adhesion of the oxide shell to the base alloy when it is exposed to oxidation and hot corrosion in different environments with high temperatures [8].

When these two conditions are met, the life of the alloy can be extended after coating it. Among the techniques used to deposit these elements as a secondary layer is electroplating, or chemical or physical vapor deposition, followed by annealing by any of the aluminization methods, which is subjected to heat treatment to produce an annealed, modified or modified layer with the desired composition. Adding active elements to high-temperature materials may improve resistance to hot corrosion and oxidation [9] These active elements are either alloyed with alloy elements or by coating to form a cover or are added in the form of oxides. Stable (oxide dispersion) or by ion implantation (lon implantation).

2. Experimental section:

The samples used were of the steel alloy known as (Steel-H25) as shown in Table (1) with different dimensions and sizes. The samples were prepared and cleaned well, as the preparation process is considered a necessary means for the coating process.

Table (1): Compositional proportions of the steel alloy known as (Steel-H25)

	Component	C	N	Si	P	S	Cr	Mn	Fe	Ni	V	Mo
	Wt.%	0.3	0.48	0.15	0.00	0.00	10.0	1.40	BAL	7.02	0.6	2.08

3. Equipment and materials used:

- The materials used are a mixture of different materials in specific weight ratios, including:

1. A mixture of pure aluminum powder (30%)
2. Ammonium chloride powder (NH4Cl) as a stimulant (4%).

3. In addition to pure aluminum oxide (AL2O3) with a weight percentage of (66%), it works to prevent the mixture from clumping.

4. The devices used are:

- A tube made of heat-resistant alumina, open at one end and closed at the other (Hodge and Dunand, 2001]
- Temperature control.
- Grinding and polishing machine.
- A sensitive electric balance with an accuracy of 0.0001gm
- X-ray diffraction (XRD) device.
- Scanning electron microscope (SEM).
- An optical microscope equipped with a camera.
- Vacuum pump
- Electric ovens reach temperatures of (1150C).

5. Sample preparation for coating:

Preparing samples is one of the important things before starting the diffusion coating process. After cutting the samples, the sample preparation process took place in several stages :

1. Performing the process of grinding and polishing the samples in order to remove the oxides present on the surface.

By using smoothing paper made of silicone with different degrees of softness, starting from (220 - 400 - 600 - 1000 - 1200) until reaching the final grade (2000)[10] [11].

2. Then the samples are washed with warm water and washing powder, then methanol to remove the stuck greasy fats, then with acetone for quick drying, then with distilled water, all to obtain a suitable surface for the coating process[12].

6. Coating Processes

Pack Cementation Coating Process

Steps

1. Prepare the pack cementation mixture:

- 25% pure aluminum powder (coating source)
- 5% aluminum chloride (activator)
- 70% alumina (Al2O3) (prevents agglomeration of the mixture)

2. Mix the mixture:

Mix all ingredients thoroughly for several hours.

3. Prepare the specimen to be coated:

Place the specimen inside the pack cementation container. Seal the container tightly on both ends.

4. Coating process:

Place the container inside a vacuum furnace. Set the furnace temperature to 1100°C. Set the coating time (2-4-6 hours).

Additional Notes

- Pack cementation is a coating process used to deposit a layer of aluminum on a substrate.
- The process is typically used to coat ferrous metals, such as steel and iron.
- The aluminum coating provides the substrate with improved corrosion resistance and electrical conductivity.

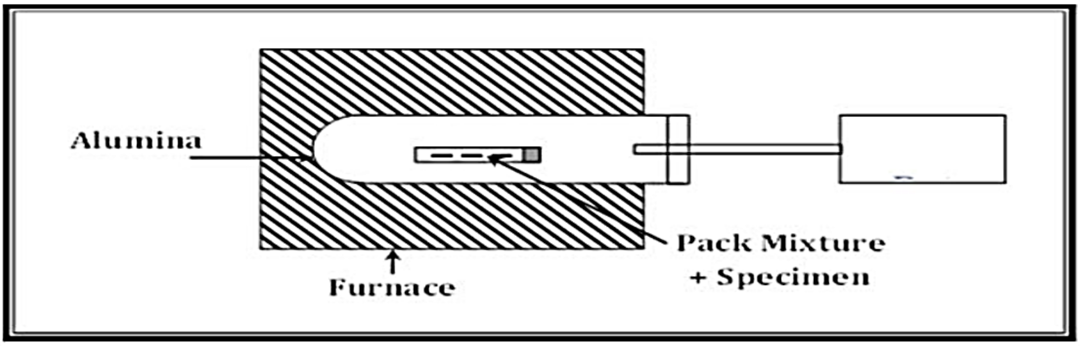


Fig. (1): represents Pack Cementation

7. Hot Corrosion: A Multifaceted Challenge for Metallic Alloys

Hot corrosion is a complex degradation process that occurs when a metal is exposed to high temperatures and corrosive environments. It is characterized by the accelerated oxidation of the metal, leading to the deterioration of its mechanical properties and a significant reduction in its service life. Hot corrosion poses a significant challenge in various industries, including aerospace, power generation, and chemical processing, where components are subjected to harsh environments characterized by elevated temperatures and highly corrosive conditions.

8. Mechanisms of Hot Corrosion

Hot corrosion involves a series of interconnected mechanisms that lead to the deterioration of the metal. Corrosive species, such as chloride salts, penetrate the metal's surface, initiating a cascade of chemical and electrochemical reactions. These reactions result in the formation of unstable and porous oxide layers, along with the development of internal voids and cracks that weaken the material's structure. The dynamics of hot corrosion can vary depending on the material's properties and microstructure, as well as the type and concentration of the corrosive species, temperature, and ambient pressure [13].

8.1 Hot Corrosion Test:

The hot corrosion test was conducted in a furnace specifically designed for this purpose using the cyclic oxidation method or thermal cycles at a temperature of (900)°C, as shown in Figure (2). The test was conducted under atmospheric pressure and each cycle lasted for five hours. This was done using an atmosphere of a mixture of sodium sulfate ($Na2SO4$) and sodium chloride (NaCl) vapor.

8.2 Test method:

A flask containing a mixture of sodium sulfate and sodium chloride with one liter of water was placed on an electric heater until it reached boiling point.

1. The vapor of the mixture was then transferred to the inside of the furnace at a temperature of 900°C.

2. This was done to test the behavior of uncoated samples and samples coated with different types of coatings, including the conventional aluminum coating (pack cementation).

Fig. (2): The system used in cyclic oxidation.

3. Weighing and measuring the dimensions of the samples: The samples were weighed before testing and their dimensions were recorded to determine the change that occurred after testing.

4. Placing the samples in a mold: The samples are placed in a mold that has cavities to hold them in place.

5. Inserting the samples into the furnace: The mold was inserted into the furnace after it reached the desired temperature (1000 C°)

6. Removing the samples from the furnace: The samples are removed from the furnace after five hours.

7. Cooling the samples: The samples are left to cool for half an hour.

8. Washing the samples: The samples are washed with water and detergent.

9. Drying the samples: The samples are dried completely.

10. Weighing the samples again: The samples are weighed again after washing and drying.

11. Repeating the process: The process is repeated cyclically for a maximum of 200 hours for testing.

12. Comparing the results: The results of the coated samples are compared with the results of the uncoated model to determine which coatings provided better protection. [14]

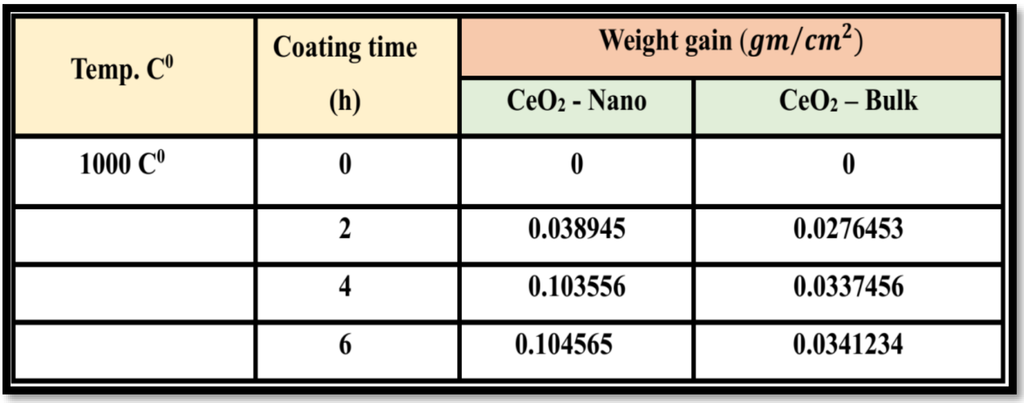
8.3 Microscopic Test:

Samples were allocated for microscopic examination after the coating processes were completed. They were subjected to cold embedding, grinding, and polishing, and then a microscopic examination was performed to determine the thickness of the coating. As for the [15] process [16] and the structures that appeared as a result of the coating, it was done using the demonstration solution, Keller's solution consists of hydrofluoric acid (1% - Hf), hydrochloric acid (1.5% - HCl), nitric acid (2.5% - HNO3), and the remainder is distilled water (95%), and To reduce hot corrosion and oxidation, the method used in our research is simple aluminized coating, or what is known as diffusion coating [17] [18].

4. Results and discussion:

Table (1) includes the results obtained from the coating operations at this degree, as it includes the weight gain rates resulting from the aluminum coating at this degree (1000) for the three coating times. Figures (2) and (3) show the presence of a parabolic relationship when plotting the weight gain rates as a function of weight sequentially Indicating that the diffusion process is the one that controls the coating process [19].

Table (2): Details of the weight gain in the presence of the thermal barrier CeO2 - Nano & Bulk) at a temperature)1000 C0)



Temp. C^0	**Coating time (h)**	**Weight gain (gm/cm^2)**	
		CeO_2 - Nano	**CeO_2 – Bulk**
1000 C^0	**0**	**0**	**0**
	2	**0.038945**	**0.0276453**
	4	**0.103556**	**0.0337456**
	6	**0.104565**	**0.0341234**

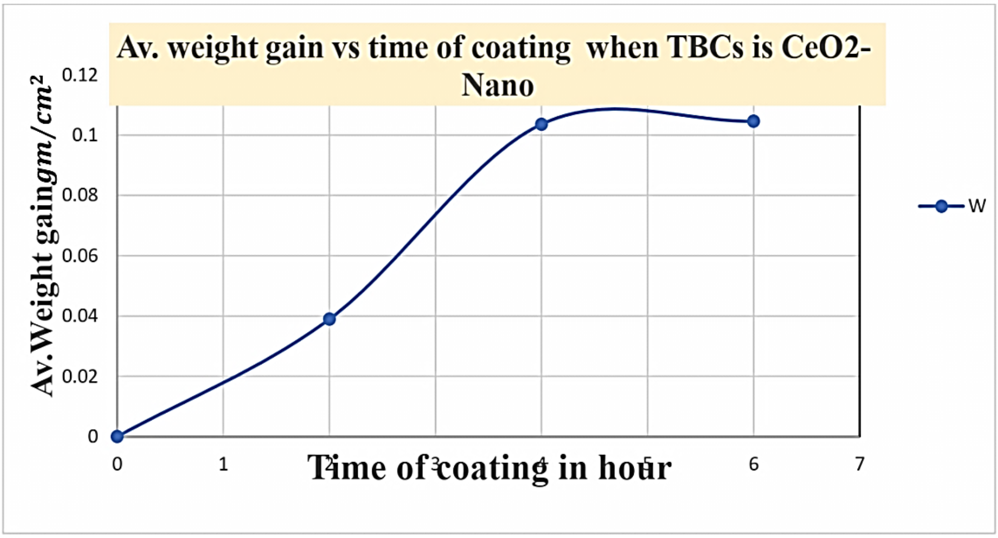


Fig. (3): The weight gain resulting from the coating in the presence of the thermal barrier (CeO2- Nano) at a temperature of 1000 C0 as a function of time

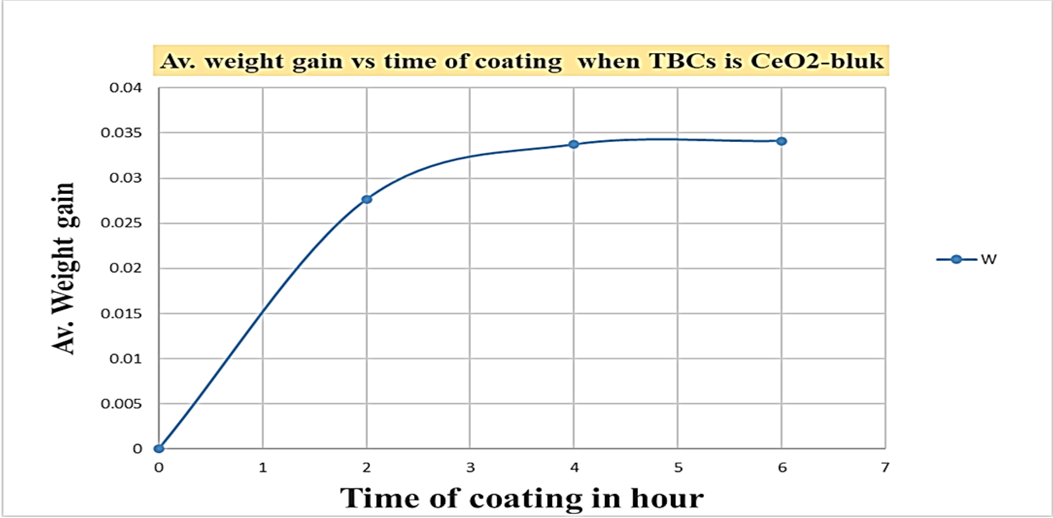


Figure (4): The weight gain resulting from the coating in the presence of the thermal barrier (CeO2-Bulk) at a temperature of 1000 C0 as a function of time

The XRD results for this coating proved that the (FeAl) phase appeared mainly at the three coating times. Table (3) shows the results obtained from the presence of very strong peaks dating back to the phase (FeAl) and strong peaks dating back to the phase (Fe2Al3). The reason for the appearance of these two developments together is that the aluminum-rich phase (Fe2Al5), which was found at temperature (1000), has begun to transform into the stable phase (FeAl). There are also weak peaks indicating the presence of what is believed to be the phase

(Fe3Al) and (Al5Cr), and the latter likely is one of the lengths deposited in the paint layers due to the limited dissolution of the chromium element in these phases. Microscopic examination: the presence of more than one phase because the display solution may attack one phase more than the other [20].

Table (3): X-ray diffraction (XRD) results for the sample coated with the thermal barrier (CeO2-Nano & Bulk) at a temperature of 1000C0 for 6 hours.

Phase type	**Relative intensity**
FeAl	Vs = (Very strong)
Fe_2Al_3	S = (Strong)
Fe_2Al	W = (Weak)
Al_5Cr	W = (Weak)
$CeAl_2O_3$	W= (Weak)

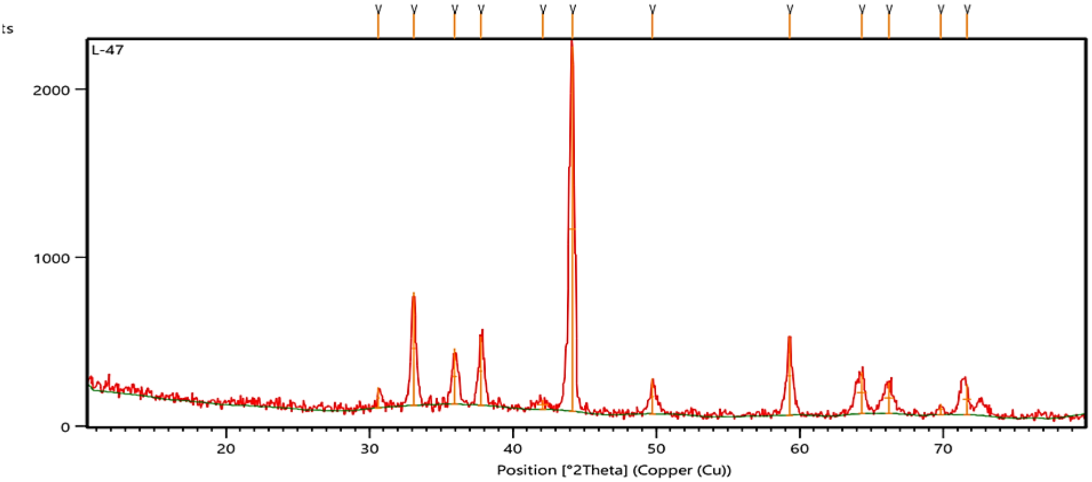


Fig. (5): X-ray diffraction diag ram of the sample coated in the presence of the thermal barrier ordinary cerium oxide (CeO2-Bulk) at a temperature of 1000 C0 for 6 hours.

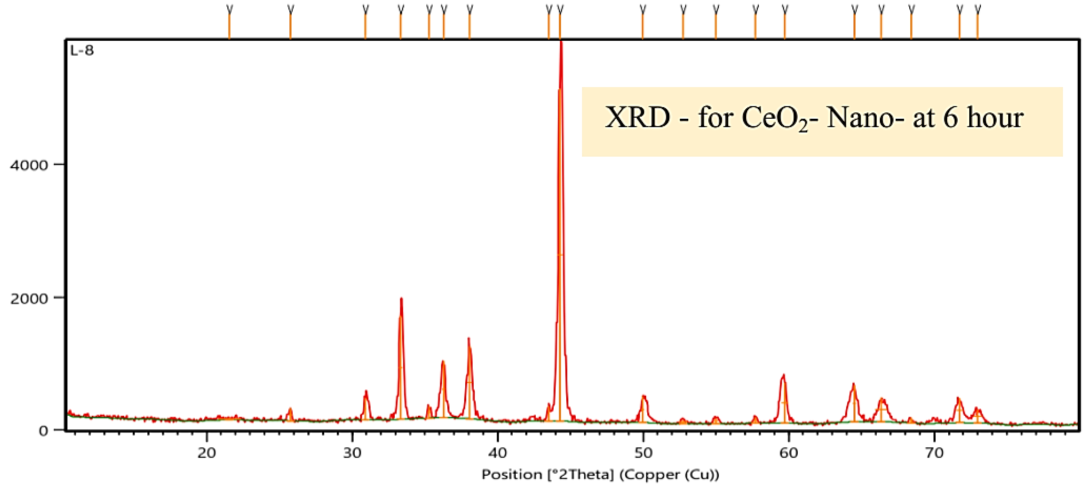


Fig. (6): X-ray diffraction diagram of the sample coated in the presence of the thermal barrier ordinary cerium oxide (CeO2-Nano) at a temperature of 1000 C0 for 6 hours.

Quantitative and qualitative analysis of sites on the paint near the surface was performed using a scanning electron microscope (SEM-EDS), as shown in Figure (6) and Table (4). The results of the examination showed the presence of a percentage of cerium (Ce) within the coating layer, and this confirms the spread of ordinary and nano cerium ions (Ce-Bulk & Nano), which are not present in the composition of the base alloy, which was shown by the scanning electron scan (SEM) in Figure (7). What was reported in the analysis using this technique is very consistent with the results obtained from X-ray diffraction analysis

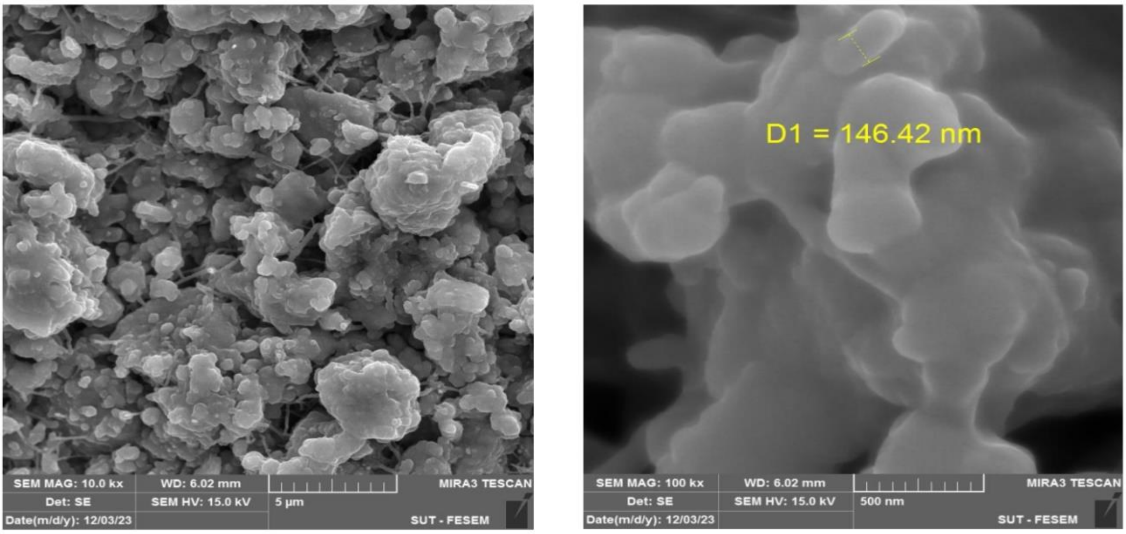


Fig. (7): Scanning electron microscopic structure (SEM) of steel alloy (Steel-H25) coated with aluminum in the presence of the thermal barrier ordinary cerium oxide (CeO2-Bulk) at a temperature of (1000 C0)for 6 hours.

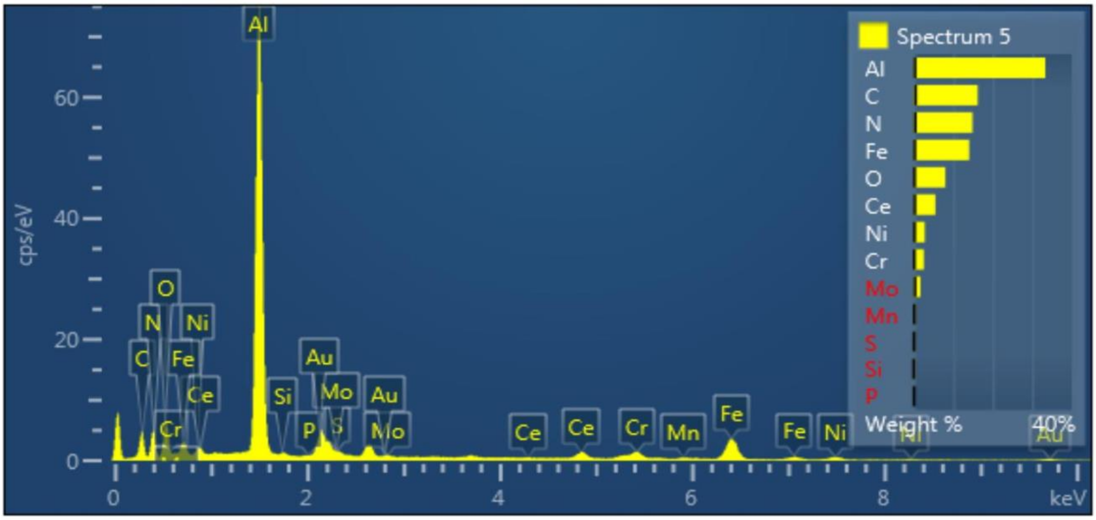
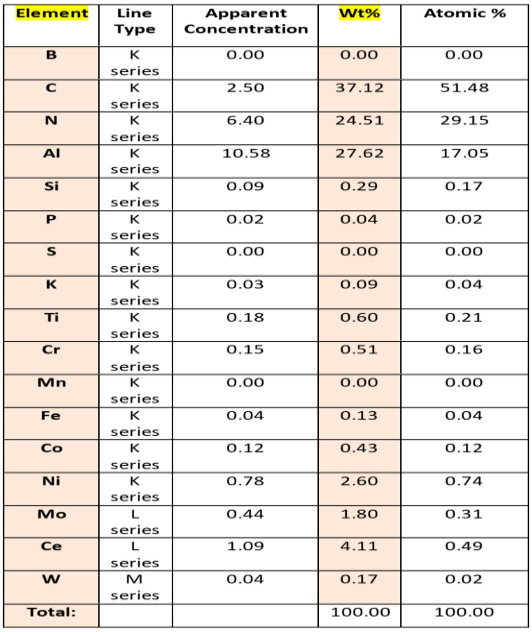
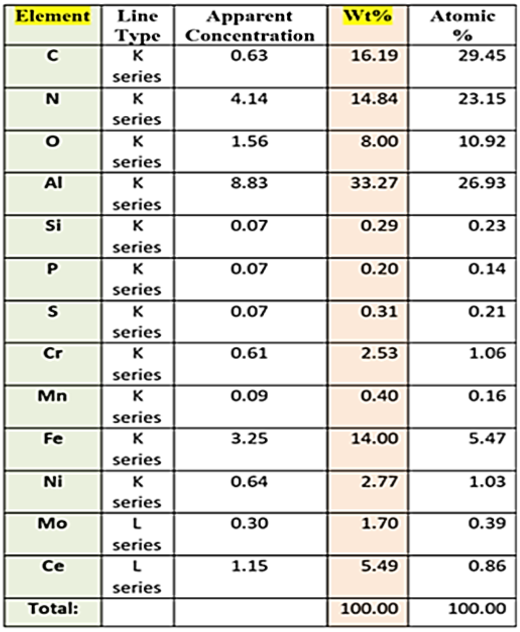


Fig. (8): Spectrogram of the quantitative and qualitative examination with the scanning electronic device (SEM-EDS) of steel alloy (Steel-H25) coated with aluminum in the presence of the thermal barrier ordinary cerium oxide (CeO2) at a temperature of (1000 C0) for 6 hours.

Table (4): Details of the weight and quality percentages in the scanning electronic device (SEM-EDS) of steel alloy (Steel-H25) coated with aluminum in the presence of the thermal barrier ordinary and nano-cerium oxide (CeO2- Bulk & Nano) at a temperature of (1000 C0) for 6 hours.



Element	Line Type	Apparent Concentration	Wt%	Atomic %
B	K series	0.00	0.00	0.00
C	K series	2.50	37.12	51.48
N	K series	6.40	24.51	29.15
Al	K series	10.58	27.62	17.05
Si	K series	0.09	0.29	0.17
P	K series	0.02	0.04	0.02
S	K series	0.00	0.00	0.00
K	K series	0.03	0.09	0.04
Ti	K series	0.18	0.60	0.21
Cr	K series	0.15	0.51	0.16
Mn	K series	0.00	0.00	0.00
Fe	K series	0.04	0.13	0.04
Co	K series	0.12	0.43	0.12
Ni	K series	0.78	2.60	0.74
Mo	L series	0.44	1.80	0.31
Ce	L series	1.09	4.11	0.49
W	M series	0.04	0.17	0.02
Total:			100.00	100.00



Element	Line Type	Apparent Concentration	Wt%	Atomic %
C	K series	0.63	16.19	29.45
N	K series	4.14	14.84	23.15
O	K series	1.56	8.00	10.92
Al	K series	8.83	33.27	26.93
Si	K series	0.07	0.29	0.23
P	K series	0.07	0.20	0.14
S	K series	0.07	0.31	0.21
Cr	K series	0.61	2.53	1.06
Mn	K series	0.09	0.40	0.16
Fe	K series	3.25	14.00	5.47
Ni	K series	0.64	2.77	1.03
Mo	L series	0.30	1.70	0.39
Ce	L series	1.15	5.49	0.86
Total:			100.00	100.00

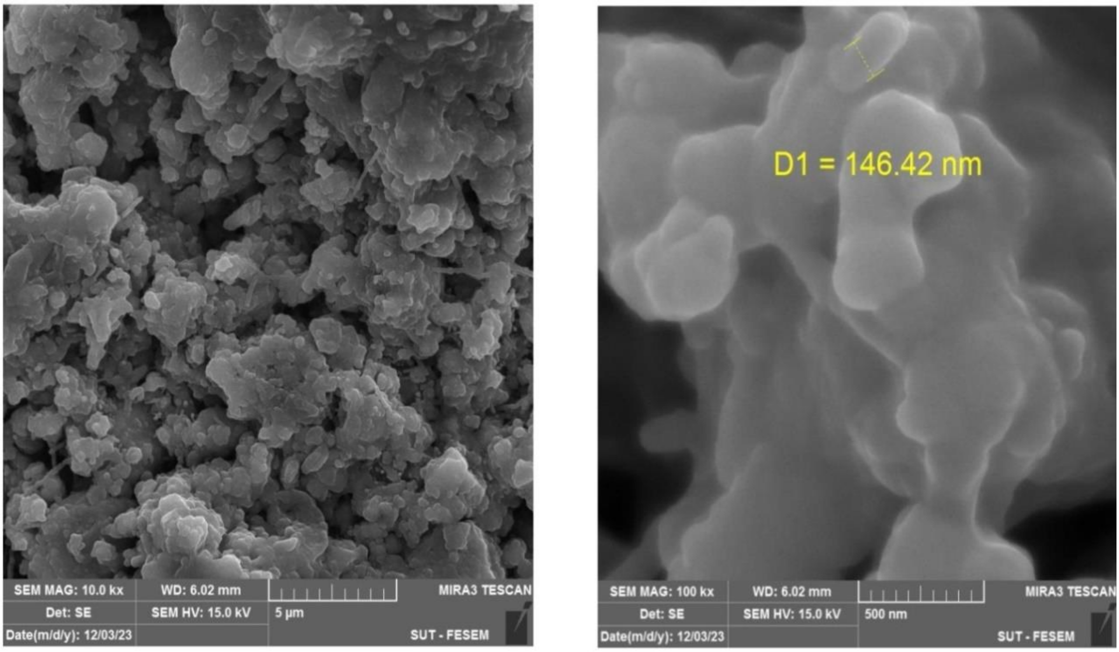


Fig. (9): Scanning electron microscopic structure (SEM) of steel alloy (Steel-H25) coated with aluminum in the presence of the thermal barrier ordinary cerium oxide (CeO2-Nano) at a temperature of (1000 C0)for 6 hours.

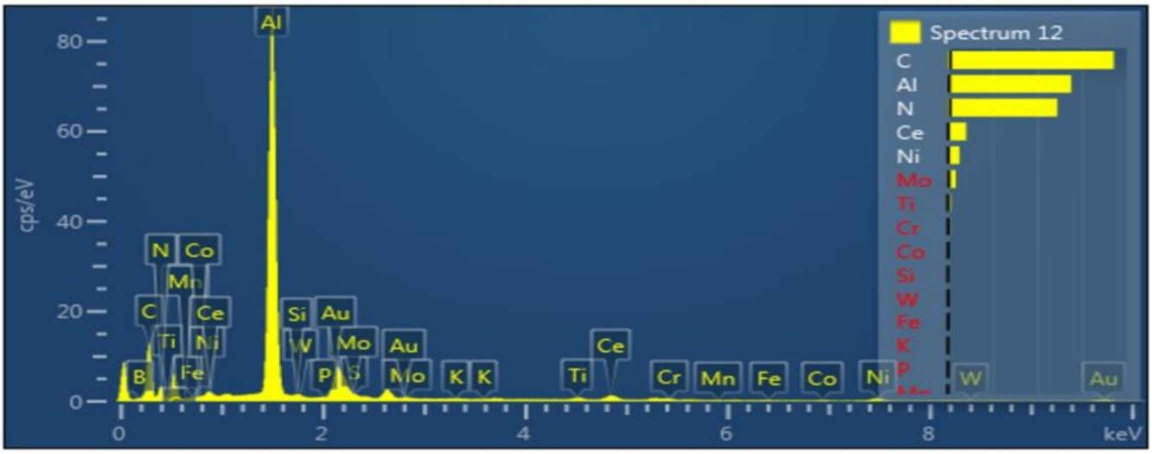


Fig. (10): Quantitative and qualitative spectrogram of the scanning electronic device (SEM-EDS) of steel alloy (Steel-H25) coated with aluminum in the presence of the thermal barrier nano-cerium oxide (CeO2-Nano) at a temperature of (1000 C0) for 6 hours.

5. Conclusion

- The weight remains stable and does not decrease approximately, especially for coating for a period of (2-6) hours until after 200 hours.
- Tests showed that the coating layer, especially at (6) hours, has good efficiency in resisting hot corrosion. This indicates that the oxide crust (Al2O3) does not fall off and that it has good adhesion.
- As for the rest of the coatings, the weight began to decrease slightly with the thermal cycles and until the end of exposure compared to the uncoated alloy, which collapsed from the first hours of the thermal cycles.
- For the plated alloy, the slight decrease in weight is due to the formation of unstable oxide (Al2O3), which is formed during transition oxidation before the formation of the protective oxide shell, Al2O3, which is formed during thermal cycles.
- It was found that the weight loss rates did not exceed 0.021gm after approximately 200 hours, and the laboratory examination indicated that the model still had good adhesion.

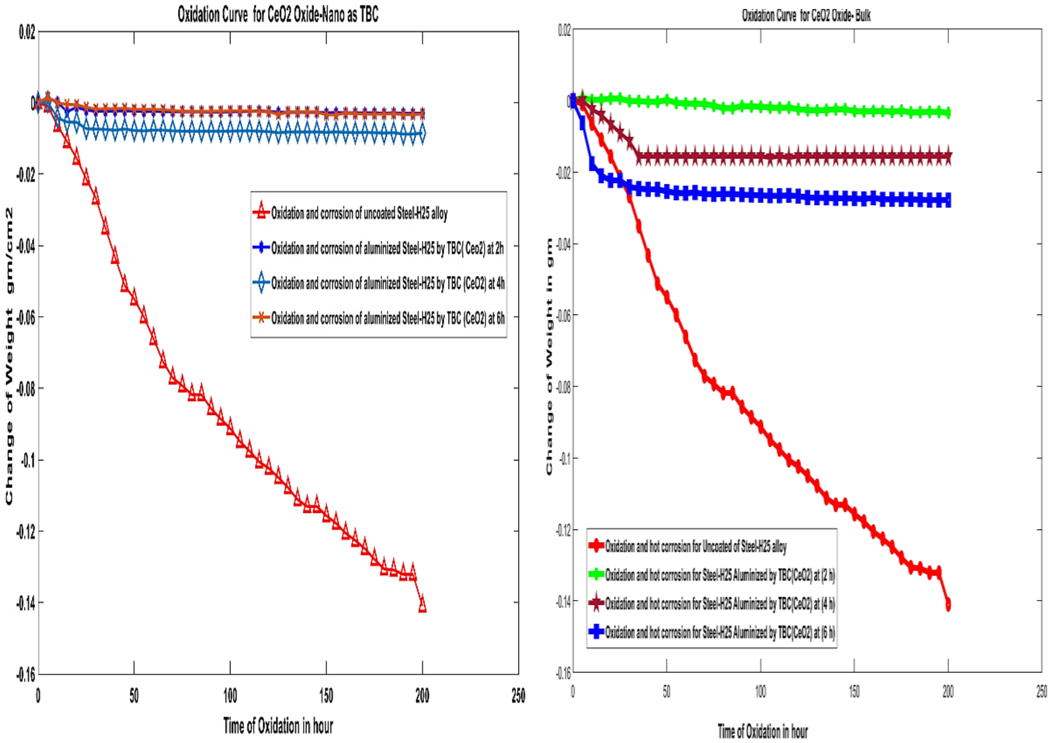


Fig. (11 & 12): show the oxidation and hot corrosion curves of the coating in the presence of the cerium oxide thermal barrier (CeO2-Nano & Bulk) for the alloy for the periods (2-4-6) hours.

References

1. Rudolph, E. M. (1987). An investigation of the hot corrosion protectivity behavior of platinum modified aluminide coatings on nickel superalloys from naval. Naval Postgraduate School.
2. Callister, W. D., (1999), "Materials science and engineering 5th ed". John Wiley and Sons, USA.
3. Houngninou, C.; Chevalier, S.; Larpin, J.P. (2003). Aluminide coatings on stainless steels by pack cementaion: High temperature reactivity. In Annales de Chem. 28, S175-S184. Lavoisier.
4. Kornilov, I. I. (1958). A high-temperature centrifuge for creep, rupture, and bend tests. JOM, 10, 187-189.
5. Squillace, P. J., Burkart, M. R., & Simpkins, W. W. (1999). Infiltration of atrazine and metabolites from a stream to an alluvial aquifer. Journal of Environmental Quality, 28(4), 1124-1130.
6. Levin, L. et al., (1998), "Controlled formation of surface layers by pack aluminization", Surface and coating technology, Vol.106, pp.209-213.
7. Mazloum, R. and G. J. T. A. o. S. Meeden (1987). "Using the stepwise Bayes technique to choose between experiments." 269-277.
8. Seal, S. and Roy, S.K., (2000), "Ceria-Based high temperature coating," ONERA, France, P.271-213.
9. Kim, K. Y., K. H. Wrolstad and F. J. G. Aminzadeh (1993). "Effects of transverse isotropy on P-wave AVO for gas sands." 58(6): 883-88.
10. Hamdan, K.E. (1983). Dimensional change due to diffusion in systems Binary. Master's Thesis, Department of Production and Metallurgy Engineering, University of Technology.
11. Al-Mazouri, H. and B. J. J. o. M. Bashi (2006). "Effect of planting dates and different concentrations of indolebutyric acid (IBA) in the rooting of the carissa's mind." 34(4): 38-48.
12. Al Taai, A. and M. J. J. o. C. o. E. Al Jubouri (2007). "On certain of differentiable equivalence of differentiable groupoids." (3).
13. Liu, D., W. Yang, Y. Chen, R. Mu and G. J. O. o. M. Tian (2022). "Hot Corrosion Behavior of a Powder Metallurgy Superalloy Under Gas Containing Chloride Salts." 98(3-4): 325-339.
14. Pint, B. A., Y. J. M. Zhang and Corrosion (2011). "Performance of Al-rich oxidation resistant coatings for Fe-base alloys." 62(6): 549-560.
15. Naim, I.S. (1990). Studying the porosity in different coating systems for low-carbon steel alloys. Master's thesis, Department of Production and Metallurgy Engineering, University of Technology.
16. Al-Hashemi, A. A. (2003). Preparation of metal coatings on stainless steel alloys (AISI-321) and their resistance to oxidation. Master's thesis, submitted to the College of Sciences, University of Mosul.
17. Zuo, Y. (1987). National association of corrosion engineering. 43(1), January 1987.
18. Eskner, M. (2004). Mechanical behaviour of gas turbine coatings, Materialvetenskap.
19. Al-Mulla, Y. A. S. (1998). Oxidation of iron alloys at high temperatures. Master's thesis, submitted to the College of Sciences, University of Mosul.
20. Morsi, K. (2001). Reaction synthesis processing of Ni-Al intermetallic materials. Materials Sci. and Engineer. A, 299(1-2), 1-15.