

Pack Cementation Coating For 304 & 316L Stainless Steel Alloys By Using Silicon Zing Process

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Abstract

In this study, we investigated the synthesis of pack cemented coating on two metallic materials (304 & 316L) in order to form silicon compounds on their surface at lower temperatures (800,900 &950°C) to avoid sintering of the pack and adhesion of material to the samples surface.

In our investigation silicon was used as a master alloy and alumina (Al₂O₃) as a filler material. Also ammonium chloride was used as an activator with different weight percentage (5,7 &10%) ,in order to increase the efficiency of the coating layer formation process. Silicon zing of two alloys which are 304 & 316L by pack cementation process according to light optical microscope examination (LOM), the coating layer formation is a temperature and activator weight percentage dependent process, which means that it is a diffusion controlled reaction. Thus the thickness of sample silicon zed with pack content 10% activator at 950°C is higher than the sample silicon zed with pack content 7% and 5% activator and these samples have higher thickness than samples coated at 900°C and 800°C at same conditions. The average coating thickness obtained by silicon zing process at 4hr by using different activator weight percentage for two selective alloys are:

- 1- 8.520 – 129.390 μm for 304 st.st alloy.
- 2- 75.929 – 192.592 μm for 316L st.st alloy.

الطلاء باستخدام عملية السلكنه باستخدام تقنية السمنتة على سبائك الصلب السباتي (304 و 316L)

الخلاصة

في هذه الدراسة تم إجراء عملية الطلاء الانتشاري بطريقة السلكنة على سبائك (304 & 316L) وهما من عائلة الصلب السباتي بدرجات حرارة منخفضة (800,900 &950°C) لغرض تكوين مركبات السليكون على سطح هذه بدون حدوث تلبيد لمسحوق الطلاء والتصاقه على سطحها. لقد تم اختيار السليكون كعنصر طلاء و اوكسيد الألمنيوم كمادة منشطة مانعة للتلبيد (حشو خامدة), أيضا تم استخدام كلوريد الامونيوم كمادة منشطة بنسب وزنيه مختلفة لغرض دراسة اثر نسبة هذا المنشط على عملية تكوين طبقات الطلاء و الأطوار الناتجة.

بينت نتائج الفحص باستخدام المجهر الضوئي المربوط إلى الحاسوب للعينات المطلوبة للمواد المستخدمة في هذه الدراسة إن طبقة الطلاء العليا تتكون من خليط من أطوار سليكون حديد وكما هو متوقع من مخطط التوازن الطوري لنظام (حديد سليكون) , هذه الطبقة تكون متبوعة بطبقة ثانية تسمى الطبقة الانتشارية والناتجة من الانتشار الداخلي للسليكون والانتشار الخارجي لعناصر السبيكة. كما إن عملية تكوين طبقات الطلاء يمكن اعتبارها عملية تعتمد على درجة الحرارة وكذلك نسبة المادة المنشطة. لذلك يكون سمك الطلاء لعينة مطلية بدرجة حرارة 950°C بنسبة منشط 10% اكبر من سمك الطلاء لعينة مطلية بنفس الدرجة ولكن بنسبة منشط 7% و 5%. وهذه العينات لها سمك طلاء اكبر من سمك الطلاء للعينات المطلوبة

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بنفس الظروف السابقة ولكن بدرجة حرارة 900°C و 800°C . أن معدل سمك الطلاء الناتج من استخدام عملية السلكنة خلال فترة زمنية ثابتة مقدارها 4hr بنفس الظروف السابقة كما يلي :

1- $129.390-8.520 \mu\text{m}$ لسبيكة 304st.st.

2- $192.592 -75.929 \mu\text{m}$ لسبيكة 316L st.st.

and 400 grit with aluminum oxide paper lubricated with water, then cleaned with alcohol, dried and then weight by using sensitive balance prior to siliconizing process.

To produce silicon compounds on these materials, siliconizing was carried out by using the pack cementation method. The pack mixture composed of ammonium chloride with different activator weight percentage (5, 7 and 10) in order to increase the efficiency of the coating layer formation process.

Also we used silicon as a master alloy and alumina as a filler material. To avoid sintering of the pack and adhesion of material to the sample surface we synthesis of pack ce($800, 900$ and 950°C). The substrate samples were embedded in the pack mixture in retort which made of stainless steel positioned in the uniform heating zone of an electrical resistance furnace, and heated to the coating temperature at constant time (4hr), as shown in figure (2).

Through the process, the argon was passed through of the retort that made of stainless steel to provide an surrounding atmosphere which prevent oxidation of the specimens and master alloy during coating process at high temperature. After each run, the furnace was cooled to room temperature while the gas continued circulating. The process time was considered to start when the retort reached the desired temperature and the process was ended when the furnace shut off. The samples were allowed to cool in the furnace ,then (after cooling), the

1. Introduction

Pack cementation is a surface treatment method which has been used ,during the last 50 years ago, for the deposition of a wide range of coating [1]. The parts which must be coated are immersed /embedded in a powder mixture held in a high temperature retort which is either sealed or else provided with a flowing inert gas (argon). The powder pack comprises on inert refractor powder, some significant amount of the element or alloy powder indented to enrich the surface by interdiffusion ,and small amount of halide activator salt [2,3, 4, 5]. The filled retort is heated to a high temperature ($800- 1200^{\circ}\text{C}$) some time according to a stepped program, where the activator salt react with the (metal / alloy) source powder to generate volatile halide species with vapor pressure corresponding to the high thermodynamic activity of the source powder [6, 7, 8]. These halide vapor then migrate in the gas phase to the part to be coated where the surface reactions, as enumerated above, resulting the deposition of the metallic component [4].

2. Experimental technique

Two substrates were chosen as base materials : 304 & 316Lstainless steel. Samples as a disc shape with diameter of (10mm), and height of (4mm), as shown in figure (1) ,were ground, smooth and flat with 260

samples were cleaned with alcohol to remove adherent pack, dried and then measured again for weight change.

* fire clay is a mixture of bauxite, kaolin and sodium silicate diluted with water, used to bond retort cover

was first cured in the furnace for (1hr) at 100°C, this procedure also served to remove water and air from the system.

3. Experimental Results and Discussion

3.1. Micro structure examination

Before microstructure examination samples were grinding at one face by using aluminum oxide paper lubricated with water (600, 800 , 1000, and 1200) grit. Then the samples polished by using (0.5 μm) alumina suspension.

After that these samples were cleaned with acetone, and will be etched by using Natal (4% nitric acid + 96% alcohol) solution. Samples immersed in the Natal for (15-20sec).

3.1.1. Average coating thickness test results for 304ss alloy

The cross – section micrograph of above samples represented by figures (4-a), (4-b) and (4-c) which show the samples treated by pack content of 5% activator weight percentage ,sample treated by pack content 7% activator weight percentage and sample treated by pack content 10% activator weight percentage about 68.52 μm , 81.49 μm and 89.814 μm thickness respectively zone effected by the cementation process seems to be composed of two layers noted. The first one represent the coating zone and the second was interdiffusion zone.

For the same condition of siliconizing treatment, but at 900°C ,figures (5-a), (5-b) and (5-c) show two coating layers also represent coating zone and

interdiffusion zone about 96.895 μm , 100.003 μm and 103.872 μm thickness respectively.

The coating layers that formed after siliconized treatment process at 950°C represent by figures (6-a), (6-b) and (6-c) which is about 111.11 μm , 120.03 μm and 129.397 μm thickness.

3.1.2. Average coating thickness test results for 304ss alloy

The cross – section samples siliconized at 800°C for 4hr represented by figure (7-a), (7-b) and (7-c) revealed a two layers coating of about 75.929 μm , 83.339 μm and 87.037 μm thickness for above treatment condition respectively. The first layer is coating zone and the second one is interdiffusion zone formed between coating and substrate. coating layers for the samples siliconized at 900°C observed by (LOM) presented in figures (8-a), (8-b) and (8-c), which are composed on two regions ,the

coating zone and the interdiffusion zone about 90.243 μm , 101.849 μm and 107.408 μm thickness for sample treated by pack content 5% , 7% and 10% activator weight percentage.

Coating layers which represented by figures (9-a), (9-b) and (9-c) for sample treated at 950°C by pack content 5% activator weight percentage. Sample treated by pack content 7% activator weight percentage and sample treated by pack content 10% activator weight percentage show only difference concerns the thickness of the cementation zone which is about 93.56 μm , 131.482 μm and 129.592 μm thickness for above treatment conditions.

However, the coating layers thickness obtained after siliconized treatment of 304 alloy thinner than that obtained for 316L alloy. Based on our observation, it is also can be concluded that the coating formation depends on:

- 1- Substrate material.
- 2- Temperature of cementation process.
- 3- Activator weight percentage and it is type.

4. Conclusions

1- The formation of silicon coatings on 304 and 316L stainless steel alloys is feasible by a single siliconizing deposition process according to the experiment results. We found that pack consisting of (5,7, and 10%) ammonium chloride and 20 % silicon as a master alloy could yield (68.520 -129.390 for 304 st.st alloy) and (75.929 -192.592 for 316Lst.st alloy) micron thickness coatings by heat treatment in range of 800, 900, and 950°C without sintering the pack mass.

2- The microstructures of coated samples show two layers of coating. The intermetallic layer consisting the intermetallic phases like (FeSi, Fe₂Si, Fe₃Si), and the interdiffusion layer. This suggests that a process in which both

inward movement of (Si) and outward diffusion of alloying elements occur.

3- The coating thickness is a temperature and activator weight percentage dependant process and it seems that the coating formation mechanism depends on the substrate which used.

5. Suggestion

1- Studying the effect of time on the coating formation mechanisms.

2- Studying the effect of inert filler material on the coating by using different materials like silica, alumina, fire clay, and sintered alumina and find the best inert material which gives rise to coat sample free from any visible particles sticking from the pack.

3- Made a comparison between siliconizing, aluminizing, and chromizing process and studying the effect of those treatments on the oxidation process and corrosion resistance.

4- Made a comparison between siliconizing process in single deposition and co-deposition with other materials and studying their influence on mechanical properties.

5- Usage pack powder with different master alloy weight percentage and studying their effect on the coating layers formation process.

6- Studying the effect of surface roughness of the sample on the diffusion process

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Table(1) coatings parameters for 304 & 316L alloys after siliconizing process for 4hr at temperatures (800,900and 950 C°)with activator weight percentage (5,7 and 10%).

| Temperature C° | siliconizing Treatment | 304 ss alloy | | | 316L ss alloy | | |
|----------------|----------------------------------|------------------|----------------------|---------|------------------|----------------------|---------|
| | | Thickness t (µm) | | | Thickness t (µm) | | |
| | | coating | Inter-diffusion zone | total | coating | Inter-diffusion zone | total |
| 800 | Treated in a pack with 5% NH4Cl | 40.745 | 27.775 | 68.52 | 57.41 | 18.519 | 75.929 |
| | Treated in a pack with 7% NH4Cl | 53.705 | 27.78 | 81.49 | 64.815 | 18.519 | 83.339 |
| | Treated in a pack with 10% NH4Cl | 69.445 | 20.370 | 89.814 | 50 | 37.037 | 87.037 |
| 900 | Treated in a pack with 5% NH4Cl | 64.815 | 31.84 | 96.295 | 62.87 | 27.66 | 90.243 |
| | Treated in a pack with 7% NH4Cl | 62.963 | 37.04 | 100.003 | 68.519 | 33.33 | 101.849 |
| | Treated in a pack with 10% NH4Cl | 66.821 | 37.051 | 103.87 | 69.815 | 42.593 | 107.408 |
| 950 | Treated in a pack with 5% NH4Cl | 74.07 | 37.04 | 111.11 | 55.78 | 37.78 | 93.56 |
| | Treated in a pack with 7% NH4Cl | 42.520 | 77.78 | 120.03 | 58.852 | 72.630 | 131.482 |
| | Treated in a pack with 10% NH4Cl | 48.967 | 80.430 | 129.39 | 114.815 | 77.78 | 192.592 |

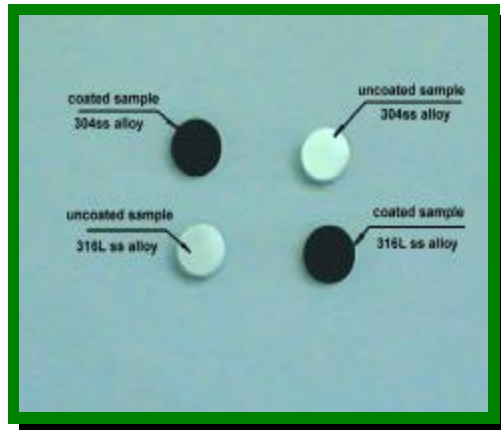


Figure (1) disc samples

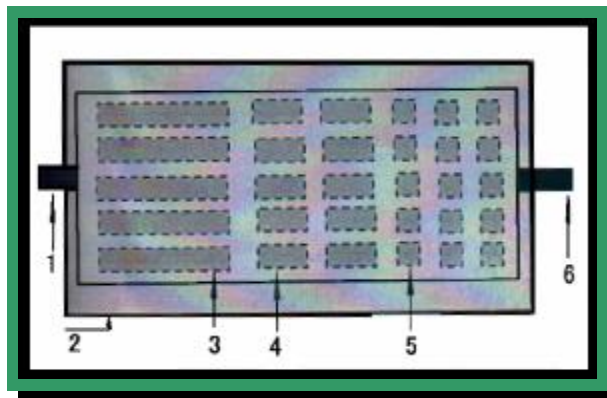


Figure (2) stainless steel retort showing the lay out of treated samples :1- inlet argon pipe 2- stainless steel retort 3- samples 4- out let argon pipe



Figure (3) retort plugged with fire clay paste inside uniform heated zone of furnace

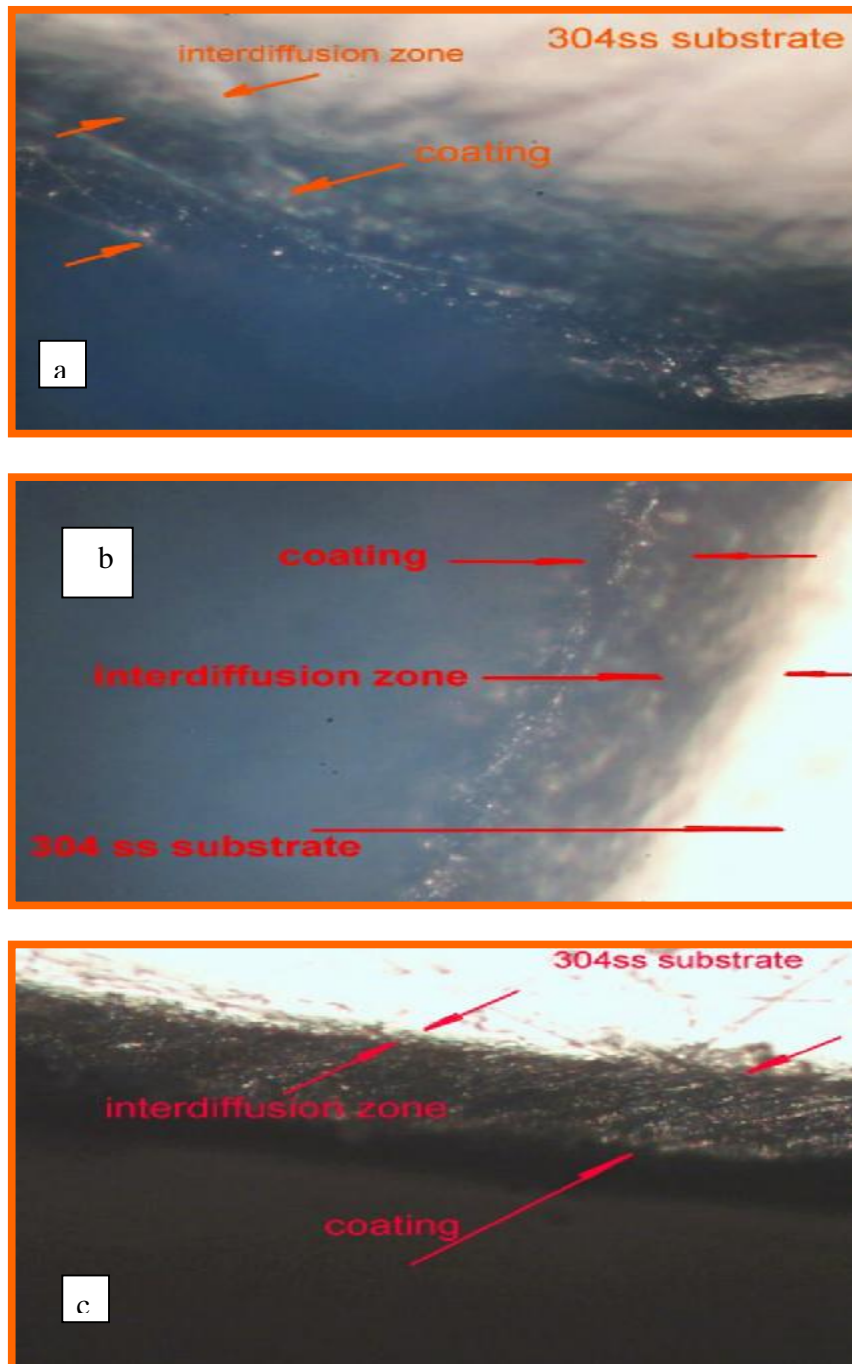


Figure (4) LOM images of 304st.st alloy siliconized at 800°C for 4hr a- for sample coated with pack activated by 5% NH4Cl b- for sample coated with pack activated by 7% NH4Cl c- for sample coated with pack activated by 10% NH4Cl

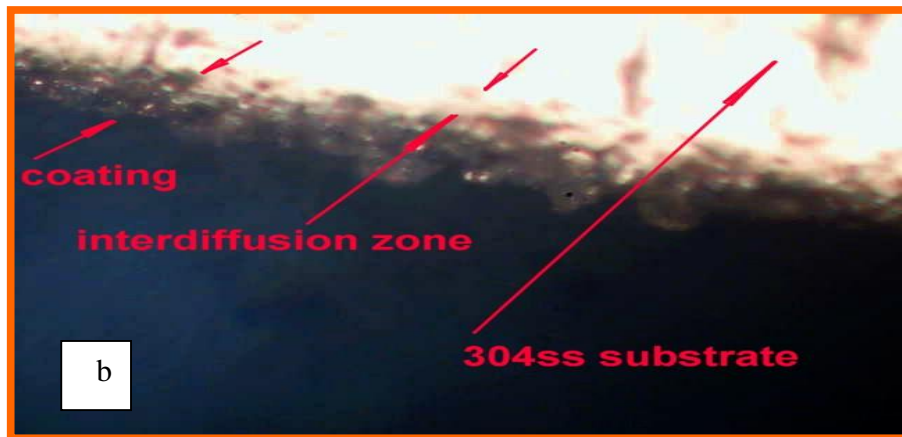
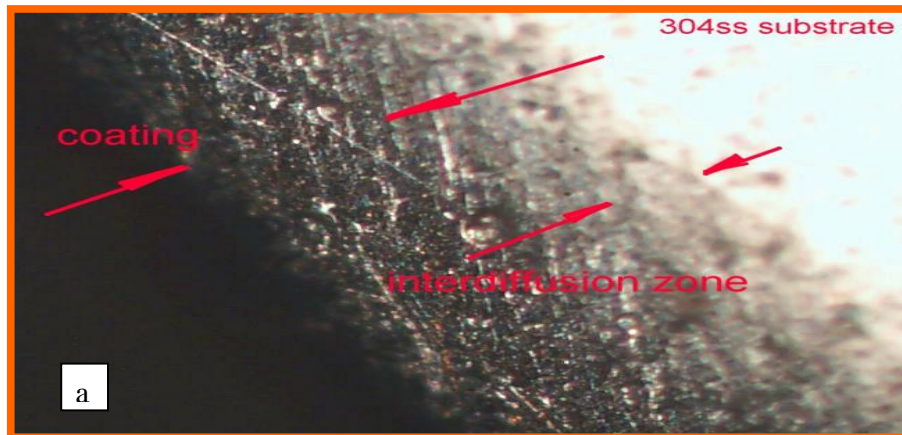


Figure (5) LOM images of 304st.st alloy siliconized at 900°C for 4hr a- for sample coated with pack activated by 5% NH₄Cl b- for sample coated with pack activated by 7% NH₄Cl c- for sample coated with pack activated by 10% NH₄Cl

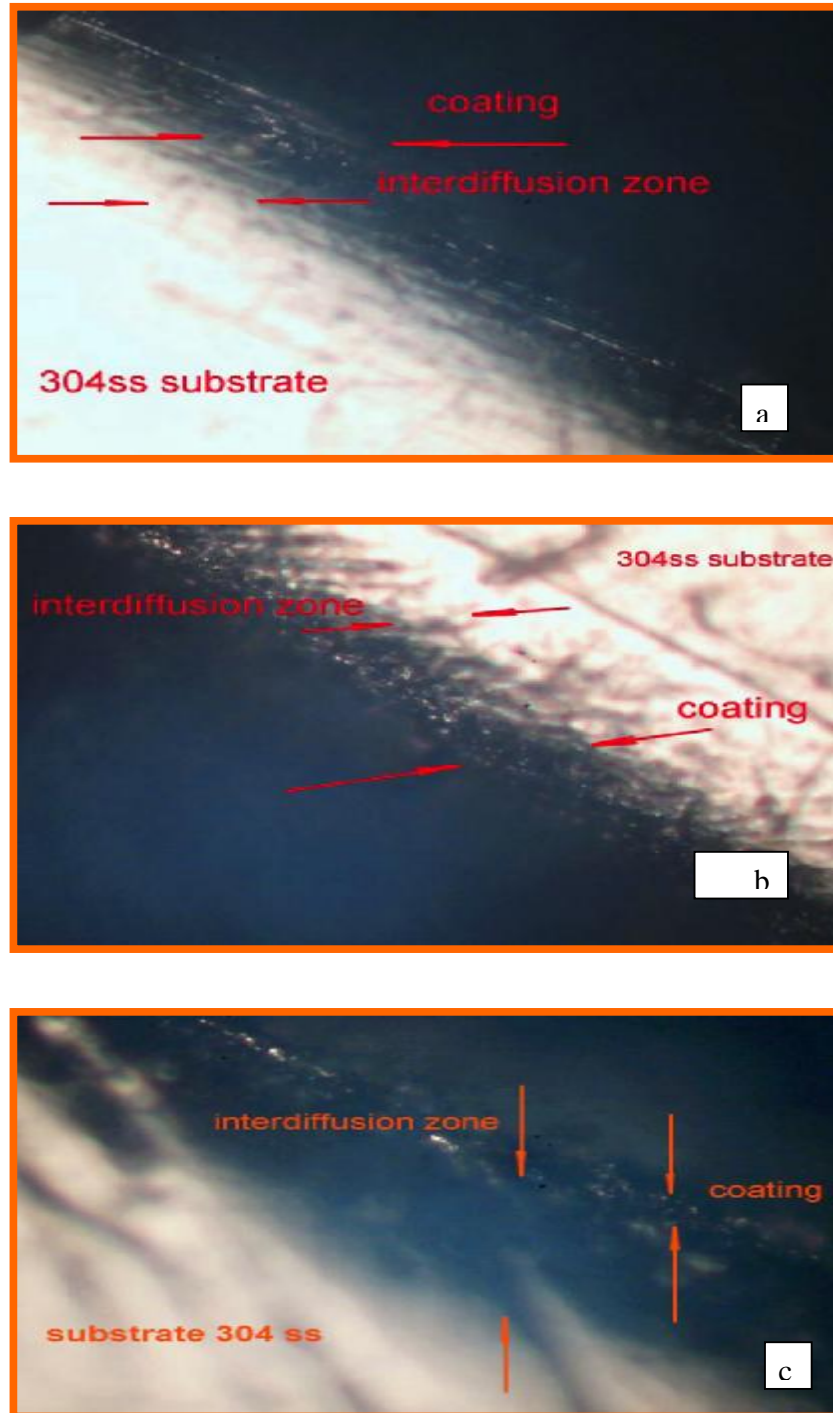


Figure (6) LOM images of 304st.st alloy siliconized at 950°C for 4hr a- for sample coated with pack activated by 5% NH₄Cl b- for sample coated with pack activated by 7% NH₄Cl c- for sample coated with pack activated by 10% NH₄Cl

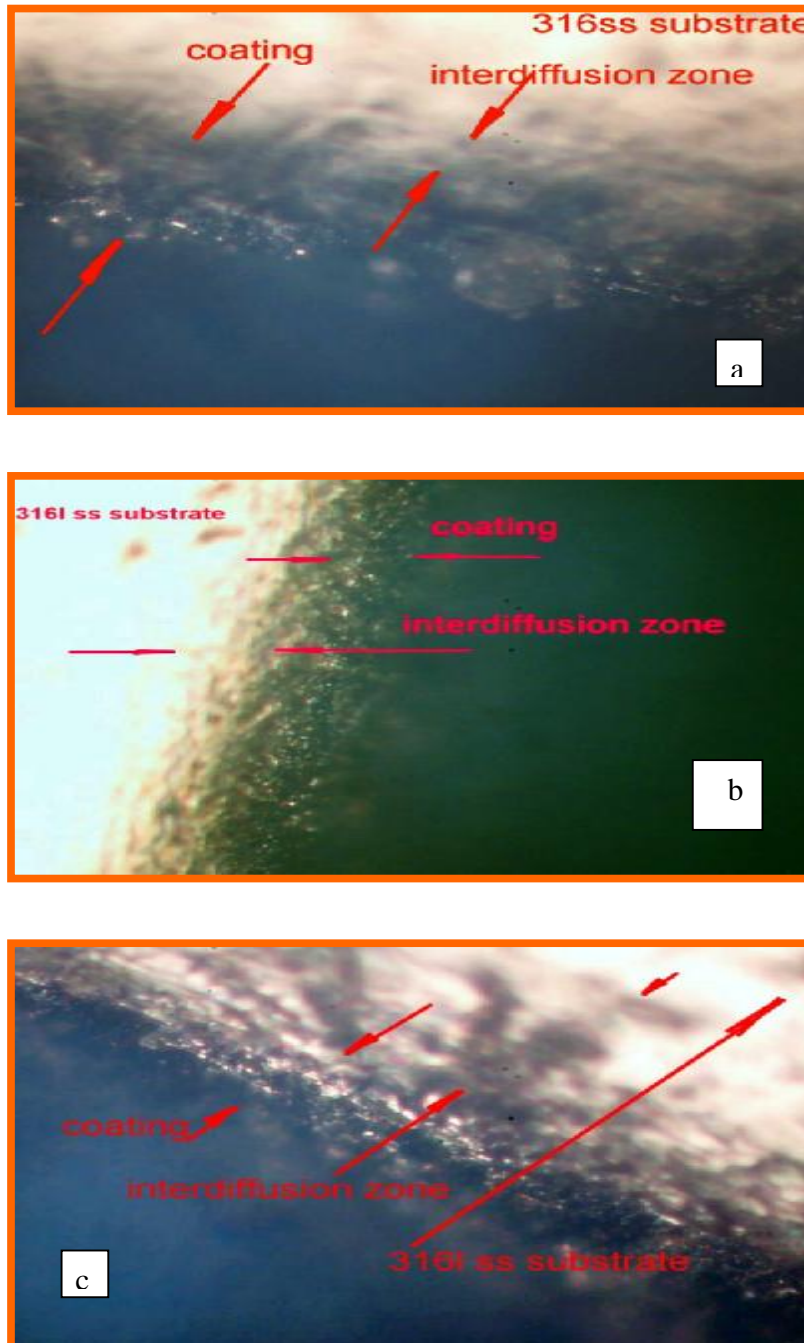


Figure (7) LOM images of 316Lst.st alloy siliconized at 800°C for 4hr a- for sample coated with pack activated by 5% NH₄Cl b- for sample coated with pack activated by 7% NH₄Cl c- for sample coated with pack activated by 10% NH₄Cl

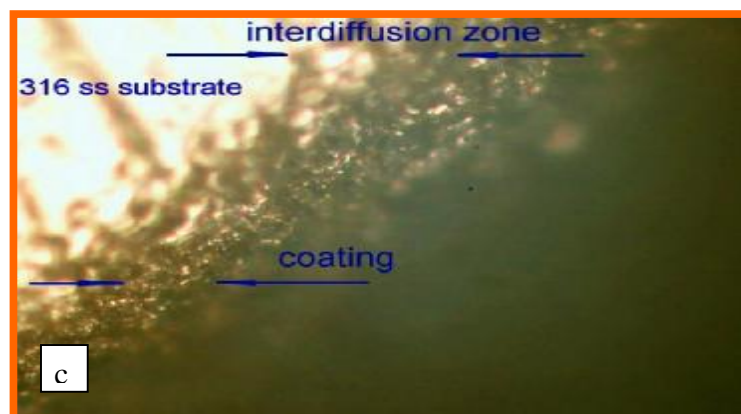


Figure (8) LOM images of 316Lst.st alloy siliconized at 900°C for 4hr a- for sample coated with pack activated by 5% NH₄Cl b- for sample coated with pack activated by 7% NH₄Cl c- for sample coated with pack activated by 10% NH₄Cl



Figure (9) LOM images of 316Lst.st alloy siliconized at 950°C for 4hr a- for sample coated with pack activated by 5% NH₄Cl b- for sample coated with pack activated by 7% NH₄Cl c- for sample coated with pack activated by 10% NH₄Cl

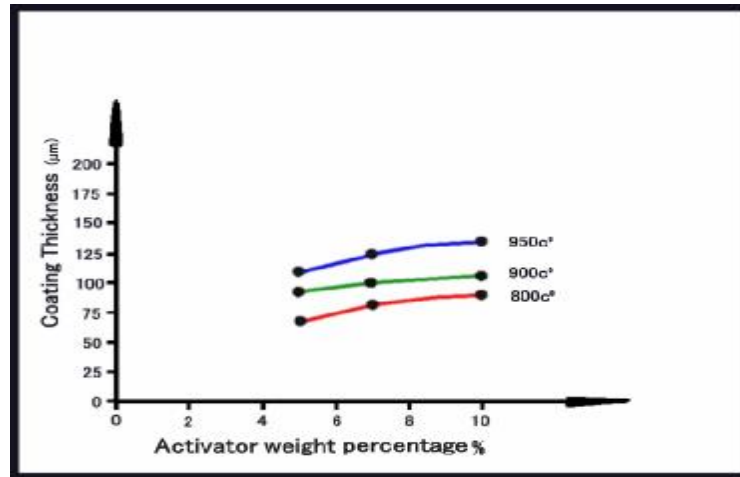


Figure (10) coating thickness variation with temperature and activator weight percentage for 304st.st alloy siliconized for 4hr

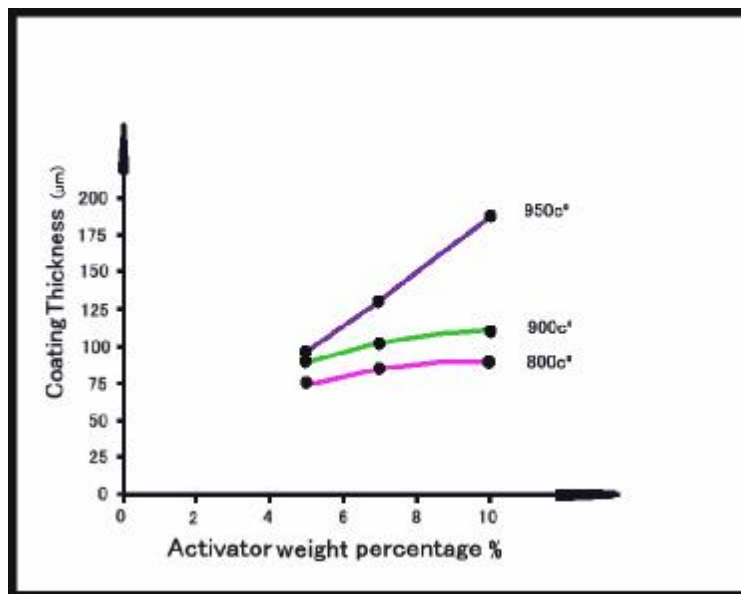


Figure (11) coating thickness variation with temperature and activator weight percentage for 316Lst.st alloy siliconized for 4hr