

Developing the Alumina Hybrid Sol-Gel Coating for Steel Oxidation Protection at High Temperatures

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ABSTRACT

The use of nano alumina thin film by hybrid sol-gel route to protect steel from high-temperature oxidation is limited due to the low thermal stability of this coat. In this work, study has been conducted to minimize this effect. The chemical compositions of solid gel (xerogel) obtained from normal alumina hybrid sol-gel were thermally varied, and then recombining with water to form the modified coating solutions at constant concentration of 0.25mol/l alumina. Laser diffraction technique has been used to measure the growth of clusters sizes in different modified solutions. X-ray diffraction analysis to characterize the alumina phase's changes as a function of temperatures. Also gravimetric weight change method to determine the oxidation rate of steel before and after coating. The results showed five changes in alumina phase during heating to 950⁰C, which are similar to that recorded for the natural ore of boehmite, and the partial removal of non stable by-products constituents associated with xerogel has considerable effect on the degree of particles aggregation and agglomeration in solutions. This worked to improve the thermal stability of the coating layer, and show considerable resistance to cracks formation. At 40-50% removal, the oxidation rate of HSLA steel specimens was enhanced by 88 % at 950⁰C compared to the steel before coating.

Keywords: Sol-Gel, Alumina, Transition Alumina, Coatings, High Temperature Oxidation, Heat Treatment.

تطوير طلاء الألومينا الجلاتيني الهجين لحماية الفولاذ من الأكسدة في درجات الحرارة العالية

الخلاصة

يستخدم طلاء الألومينا النانومتري بطريقة المحلول الجلاتيني الهجين لحماية الفولاذ من الأكسدة بدرجات الحرارة العالية بشكل محدود بسبب محدودية استقرارية هذه الطبقة. في هذا البحث، تمت دراسة التقليل من هذا التأثير، إذ تم تغيير مكونات تركيبة الجلاتين الصلب المستحصل من محلول الألومينا الجلاتيني الهجين الاعتيادي حرارياً ثم إعادة تشنيتته في الماء لتكوين محاليل طلاء مطورة بتركيز 0.25mol/l ألومينا. استخدمت تقنية الحيود الليزرية لقياس حجم نمو عناقيد الجسيمات النانومترية في هذه المحاليل، وتحليل حيود الأشعة السينية لتوصيف التحولات الطورية للألومينا بدلالة درجة الحرارة. كذلك استخدمت طريقة اعتماد الفرق الوزني للنماذج في احتساب معدل الأكسدة قبل

وبعد الطلاء. بينت النتائج حصول خمسة تحولات طورية للألومينا خلال التسخين إلى 950°C ، هذه الأطوار تقارن بتلك المستحصلة لحام البوهمايت الطبيعي ، وان التخلص الجزئي للنواتج العرضية غير المستقرة من تركيبة الجلاتين المجفف يغير من مدى تجمع وتكتل الجسيمات في المحلول، وبالتالي يحسن من الاستقرار الحرارية لطبقة الطلاء ويظهر مقاومة واضحة لتكوّن التشققات . عند بلوغ نسبة إزالة 50% أظهرت نتائج فحص الأكسدة عند 950°C تحسن في معدل الأكسدة لنماذج الفولاذ منخفض السبائكية عالي المقاومة ، بعد طلائها بمحلول الطلاء المطور، بمقدار 88% عما كان عليه المعدل ما قبل الطلاء.

INTRODUCTION

A Special new application for Sol-gel derived ceramic coatings is the protection of steel against formation of scale during the hot forming at 950°C . This process is a new production in the automotive industry. The strength of steel is enhanced by this process, hence the same mechanical stability can be achieved with lower sheet thickness, and in this way the weight of the car is reduced [1]. HSLA steels are increasingly replacing traditional low carbon steels for many automotive parts. This is due to their ability to reduce weight without compromising strength and dent resistance [2]. However, corrosion protection of actively corroding metals such as iron/ steel using such methods remains relatively less explored, specially the protection from oxidation at high temperatures. Many difficulties have been mentioned for this type of application, as the fast thermal pyrolysis of organic components in the coating [3], the formation and interference of non-protective rust during the coating process [4-5], and the insufficient thermal stability due to residual stresses which result in cracks formation [6-9]. A recent study [10] concluded that, the whole variation of residual stress in a sol gel coatings with heating temperature could be understood in terms of film densification, structural relaxation, atomic diffusion, progress of crystallization and thermal strain.

In this work, the chemical composition of alumina hybrid sol-gel prepared from organic and inorganic precursor of aluminum isopropoxide and aluminum chloride respectively were varied through heat treatment of xerogel from this solution to different removal percent of by-products which are mainly aluminum chloride and organic compound, then the treated xerogel dissolved in water to form the modified coating solutions. Laser diffraction technique used to measure the growth in clusters sizes in different modified solutions. X-ray diffraction analysis used to characterize the alumina phase's changes as a function of temperatures, and gravimetric weight change method to determine the oxidation rate of HSLA steel specimens before and after coating in term of different modified solutions.

Experiment

Preparation of organic alumina sol-gel: The sol was prepared by hydrating aluminum isopropoxide ($\text{Al}(\text{OC}_3\text{H}_7)_3$) with distilled water in a molar ratio of 1:90 (isopropoxide to water) at about 85°C with stirring for 1 hr using magnetic stirrer, and then few drops of the nitric acid was added into the solution to adjust the pH value to about 3~5 [11], and complete hydrolysis process according to the reaction in the following equation (1) [12]. The concentration of alumina in the final solution was $0.25 \text{ mol} \setminus \text{L}$.



Preparation of inorganic alumina sol-gel: the sol-gel synthesis consisted of adding 30 gm of 28% ammonium hydroxide solution to 10.66 gm of 0.1M aluminum chloride

solution. 800 ml of distilled water gradually added with vigorous mixing at 90⁰C for 10 hours. The gel was let to mature for 24 hours at room temperature to complete the transformation to gel state [13] according to reaction in equation (2), as follows:



Preparation of hybrid solution: to create a hybrid solution coating the two solutions of organic and inorganic were mixing by volume ratio of 4:1 respectively, leaving for a period of three weeks for Aging.

Drying of hybrid solution: to separate the constituents of the sol-gel solution in solid (Xerogel), slow oven drying for one hour at 80⁰C was applied and then for half an hour at 100⁰C to achieve fully drying.

Preparation of developed coating solutions: the xerogel divided into six parts of 2.5 gm for each one. Furnace treatment was conducted on five for 5,10,15,20 and 30 minutes at 220⁰C. The sixth part dissolved directly in water for reference. Weight change in each part recorded for percent removal of unstable by product constituents calculation, then each sample dissolve in water to get the developed solution of 0.25mol/l alumina concentration.

Preparation of substrate: specimens of 18x20x2mm size were cut from high strength low alloy steel (HSLA) plate of nominal composition (in wt. %) C-0.409, Si-0.08, Mn-0.42, Ni-0.142, Al-0.063, Ti-0.079, Cr<0.05, Mo<0.05, Cu<0.05, Co<0.05, Nb<0.05, V<0.05. The specimens were ground successively on 600µm emery papers grit followed by degreasing with ethanol and finally cleaned with distill water. Recent work [14] shows that, the sol-gel without prior conversion coating on steel results in poor corrosion protection due to formation and interference of non-protective rust during the coating process. This result is consistent with the latest works [4-5] as used conversion coating prepared from oxy aluminum hydroxide and before that a layer of zinc phosphate used as treatment prior to the sol gel coating to prevent the formation of rust and to increase the adhesion strength of to the surface [15-16]. To improve the performance of sol-gel coating, (HSLA) steel specimens were therefore coated in two steps:

- Conversion coating which seals the surface to provide good template for the subsequent sol-gel alumina based coating and,
- Developed alumina based sol-gel coatings for enhancement of corrosion and oxidation protection. The methodologies of coating fabrication on (HSLA) steel specimen are discussed in the following :
- Conversion and sol-gel coating: The Conversion coating solution [14] was prepared by drying the solution of organic alumina gel, then thermally treated the remaining solid gel (Xerogel) to 170⁰C for half an hour and dissolving in distilled water to get a 0.25 mol/l alumina concentrations ,then 0.5N NaOH add to adjust the solution PH to a value of ≈8 .This solution, then applied on HSLA steel specimens using dipping technique by immersing for two minutes in a vertical to reach the substrate-solution phase boundary equilibrium [17] , then at a constant withdrawal speed of 10 mm/min and dried for 24 hours in ambient atmosphere. The dip-coated specimens were heated at rate 1.5⁰C/min to 400⁰C for half an hour for sintering, followed by furnace cooling. After cooling, the specimens were cleaned in ethyl alcohol. Specimens then coated in the same procedure for developed and conventional alumina hybrid coating to be ready for oxidation test.

Oxidation test: To stand on the protective properties of coating deposited on HSLA steel specimens and its effectiveness in providing protection to the substrate from oxidation at high temperature, oxidation test were conducted before and after coating in an electric furnace at 950⁰C for one thermal cycle oxidation test (heating – on temperature- cooling) in normal furnace. The heating time and test time were one hour each and two hours for cooling and the specimen's weight-change measurement in terms of exposure time used as indicator for the rate of oxidation, by using an electronic balance of pointed sensitivity 0.1mg. In accordance with the relationship in equation (3) which define the oxidation rate (S) as the amount of the increase in the weight of specimens per unit surface area in terms of exposure time [6], the value of comparison between different coatings performance will adopt from the ratio between the oxidation rate before and after the coating and the percentage improvement in protective properties offered by the coating layer as can be calculated from the relationship (4) and (5):

$$S = \Delta m / A \quad \dots (3)$$

$$R = S_{\text{coated}} / S_{\text{uncoated}} \quad \dots(4)$$

$$OR\% = 100(1 - R) \quad \dots (5)$$

S: oxidation rate (mg/cm²), **Δm**: specimens weight change (mg), **A**: specimens surface area (cm²), **R**: protection ratio, **S_{coated}**: oxidation rate after coating, **S_{uncoated}**: oxidation rate before coating, **OR%**: percentage of oxidation rate improvement. When the value of **R** approaching zero, the protection provided by the coating layer in the best and when approaching the value of one, then coating do not provide any protection to the steel substrate and between these limits protection properties ranging in different proportions to reflect the effectiveness degree of the coating in minimize the oxidation process.

X-ray diffraction (XRD): To evaluate the phase's changes in coatings adopted from developed coated solutions up to oxidation test temperature. XRD peaks were obtained in Shimadzu XRD-6000, operating with copper K-gamma radiation at 40 kV and 30 mA, the scanning was conducted for all specimens between (2θ) =20 and (2θ) = 60, a speed of 5 degrees per minute.

Laser Diffraction Particle Size analysis: Laser Diffraction Particle Size analyzer of the type (SALD-2101), measured extent 0.03 and 1000 microns used to measure the sizes and distribution of particles and/or clusters of particles in coating solutions as a function of the removal percent of unstable constituents as a result of varying the heat treatment time.

RESULTS AND DISCUSSIONS

Developed coating solutions properties: Table (1) shows the xerogel granular obtained from drying the alumina hybrid sol-gel which consists of the products of reactions in equations (1) and (2) , aluminum oxide and by-products constituents as ammonium chloride with organic compounds which sublimate and/or decompose at range of 170 -338⁰C. The table also shows the proportions of these components as calculated by assuming complete reactions, it's clear that the importance of these by-products which accounted for 76.4 % of entire composition, these components are

practically considered as unstable and usually disposed on sintering stage after applying the coating later on steel substrate. The post partial removal of these materials by gradual heat treatment up to 220°C showed the following results:

- Figure (1) shows the obtained non linear function of by-products removal percent in term of thermal treating time. It is clear that 80 % of these materials are removed by slow heating for 30 minutes. This function considered as mainstay for the process of producing different coating solutions of different protective performance as it will be detailed later.
- Figure (2) shows the non-linear relationship connecting the xerogel by-products percent removal and average particles clusters size at 50% of total amounts (median D_{50}) adopted from the laser diffraction analysis, through this function, one can expect the achieving clusters size and their distribution to developed coating solutions, and together with function in Figure (1) worked as integrated knowledge for xerogel heat treatment process operation at temperature not exceeding 220°C.
- Figure (3) presents the detail laser diffraction analysis of the clusters size distribution in the five developed solutions of 10.2, 21.8, 42.1, 68.5 and 80% by-product constituents' removal percents. It is clear that gradual removing of these materials to more than 20% lead to aggregate and agglomerate particles in the solution with micro-size up to 8.3 μm , while 20% removal or less worked to stay clusters at size in a range of less than 840nm. This result reflects the important role of these constituents in developing solutions of different particles agglomeration degree which controlled through the time of a slow heat treatment process of xerogel.
- Relying on the output in Figure (3), these results are advance to that exhibited by recent work [14] which used the function of changing the acidity of alumina hybrid coating solution to build highly branched polymeric structures clusters in different sizes up to less than 2 μm at D_{50} . The achieved process in this work is more capable to control the sizes limits of these clusters, as they reached 6.907 μm at D_{50} , based on the philosophy of developing the sol gel of nano properties to either colloidal dispersion and/or suspension properties without using any additions of pre-prepared nano materials particles which claim to increase coating layer cohesion and adhesion to substrate and minimizing the possibility of cracks formation during the early thermal treatment stage at range 400-500°C [18].
- The obtained xerogel granular after different thermal treatments at a temperature not exceeding 220°C, form with water instant coating solution. However, the practical points of view indicate the need for much vigorous mixing as the percent removal of by-product increased. This case physically related with the degree of particles aggregation and agglomeration in coating solution according to the mechanism illustrated schematically in Figure (4).

Densification treatment up to 400°C: Figure (5) shows the results of the X-ray diffraction analysis of the xerogel after heat treatment up to 400°C. The following results were obtained:

- Figure (5-a) shows the existence of crystallized phases of aluminum oxy hydroxide and the residual amount of ammonium chloride after 10 minutes treatment at 220°C.
- Figure (5-b) shows complete elimination of ammonium chloride, disappearance of aluminum oxy hydroxide and no significant presence of any alumina crystalline phase, which means that, the transformation toward the amorphous phase

(Al₂O₃amorphous) occurred as shown by equation (6), these transformations compared to that for natural ore of boehmite which correspond to chemical composition of Oxy aluminum hydroxide [20-22].



The above discussed results reflect the extent of the changes in the coating composition, structural change and phase transformation in this stage of densification treatment, which all together effects to the integrity of growing coating layers , for that the current trend concentrate towered minimizing these impacts by partial removal of unstable constituents for better relaxation.

Tracking of Transitions alumina phases at 400-1000⁰C: Figure (5-c,d,e) revealed the XRD powder patterns for the amorphous alumina derived from equation (6) after half an hour treatment at 700⁰C, 900⁰C and 1000⁰C, the obtained patterns match those of δ , θ γ -alumina of standard spectra files 10-0425,04-0877 and 11-0517 respectively [21], thus the following equation (7) with equation (6) completed all Alumina phases transformations obtained from developed hybrid coating solution up to 1000⁰C as follows:



The number of transition alumina, their types and its existence temperature range are determined by the type of the starting precursors, they are different for crystalline hydrates of aluminum salts [21]. However, boehmite and the xerogel prepared in this work from organic and inorganic precursor of aluminum isopropoxide and aluminum chloride respectively are the highest in transition alumina numbers; accordingly their distractive effects should be the highest as well. The occurrence of four transformations in phase for coating applications at temperature between 220⁰C and 1000⁰C shows the need to limit their impact on the coating integrity. The crystallite size increases, and this increase being more important in the case of the organic precursor [13]. However, in general these phenomena result in building considerable stresses along with that stresses generated thermally in the coating layer during densification treatment as discussed before, leading to induce cracks and thus reducing the protective properties of coating, and this is, what this work sought through the development of conventional sol-gel to minimize these effects through controlling the proportion of the unstable constituents in coating layer which is the most effective parameter as the oxidation test will show.

Qualitative properties of oxidation: To stand on the effectiveness of the developed hybrid sol gel coating to show their protective properties compared with the conventional coating solution, the following results were obtained from the oxidation test of coated specimens at temperature of 950⁰C for one hour in the normal furnace air without prior conversion coating:

- Cracks formation and spalling led to the fragmentation of conventional hybrid coating, as can clearly seen in Figure (6-a). The surface morphology of the coating layer seen in Figure (7-a) , reveal surf like as a result of stresses effected their cohesion leading to cracks formation and air ingress to the steel surface freely causing rapid oxidation. Figure (7-b) showed the nodular morphology of the under coat

oxidation products. These results again explain the need to the more structural relaxation to minimize the distractive effects of residual stress.

- Specimens coated by developed hybrid sol gel with prior removal of 68.5% by-products from sol gel showed more stable morphology as did not shows visual cracks even after cooling, although the coating layer deformed in the middle by swollen for 4 mm, compared with the specimen length of 18 mm and 14 mm width, which means that the percentage of deformation in coating layer at length and width directions are 2.4% and 3% respectively.

- Figure (6-b & 6-c) illustrated schematically this result which reflect the suitability of these developments to relax the coating structure, therefore, we based on this result to scan oxidation properties of different removal percent of by-products constituents from xerogel producing optimum coating for high temperatures applications with maximum oxidation protection.

The same test was applied with prior conversion coating in term of different removal percent of sol gel by-products constituents, the following results were obtained:

- Non linear relation between the deformation degree of coating layer in terms of spalling, elasticity and cohesion, and removal percent of sol gel by-products constituents. Figure (8) showed generally these differences in specimens view after test, as at 40-50 % removal and average particles clusters size at 50% of total particles amounts (median D_{50}), of $D_{50} = 1.420\mu\text{m}$, the specimen (c) shows the best performance.

- The prior conversion coating were effective only with limited region of particles clusters size to enhance the adhesion of coating layer to the specimens surface.

- Figure (9) reveal a homogenous surface morphology of coating surface for the specimen in Figure (8-c), as can be seen, free of defects that noted for others.

Quantitative properties of oxidation: Figure (10) and Table (2) shows the variation percent of oxidation rate in terms of increasing the size of particles clusters at different removal percent of the by-products constituents in coating solutions, as can be seen the relation is not linear and the maximum reduction of 88% in oxidation rate was obtained at 42.1% removal percent and at average cluster size $D_{50} = 1424\text{nm}$, this result can be discussed as follows:

- The by-products constituents are water soluble acting as carrier for the insoluble alumina particles, so the partial removal of these carrier lead to increase the agglomeration of these particles into clusters of bigger size as explained in Figure (1, 2 and 4). This case offered suitable and/or optimum condition to the coating structure to relax as the temperature increase to the test value at 950°C , thus minimizing the effects of the normal thermal residual stress and that build up as a result of alumina crystallization progress and transient phase changes, which are the important process in cracks inducing mechanism.

- Prior partial removal of the by-products from the coating solutions help to minimize the bulk of coating densification by sublimation and decomposition processes of these constituents, thus their mass transfer across the coating layer approach to the optimum value that leave minimum porosity acting as free path for oxygen diffusion to the substrate/coating layer, in this case the reduction in oxidation rate will be at maximum value.

- The maximum obtained reduction in oxidation rate compared to that before specimens coating was 88% which equivalent to 8~9 times.

Process summery

Figure (11) presents the current process flow diagram for developing the alumina coating solution from the mother hybrid sol-gel.

Table (1) Constituents of xerogel deposited from drying the hybrid alumina sol gel and the limit of thermal Stability of each.

	stability	Weight %	constituents
	loss of crystalline water at 250-550 ⁰ C,unstable up to 1100 ⁰ C	23.6	Al ₂ O ₃
	Sublimate and decomposed in temperature range 200-338 ⁰ C	33.2	NH ₄ Cl
	Sublimate and decomposed in temperature range 150-170 ⁰ C	43.2	(CH ₃) ₂ CHOH

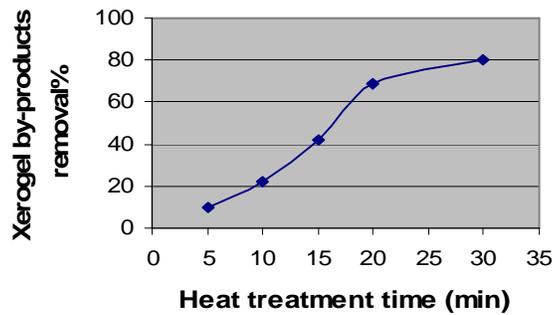


Figure (1) Percent removal of unstable by-products from xerogel as a function of heat treatment time at 220⁰C.

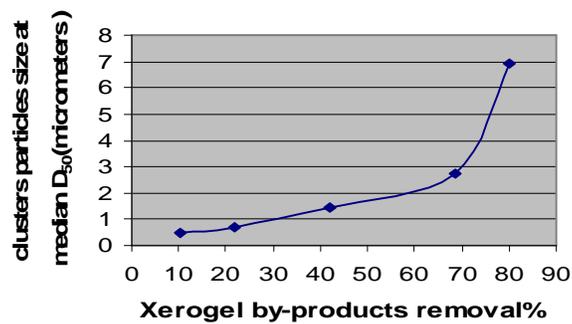
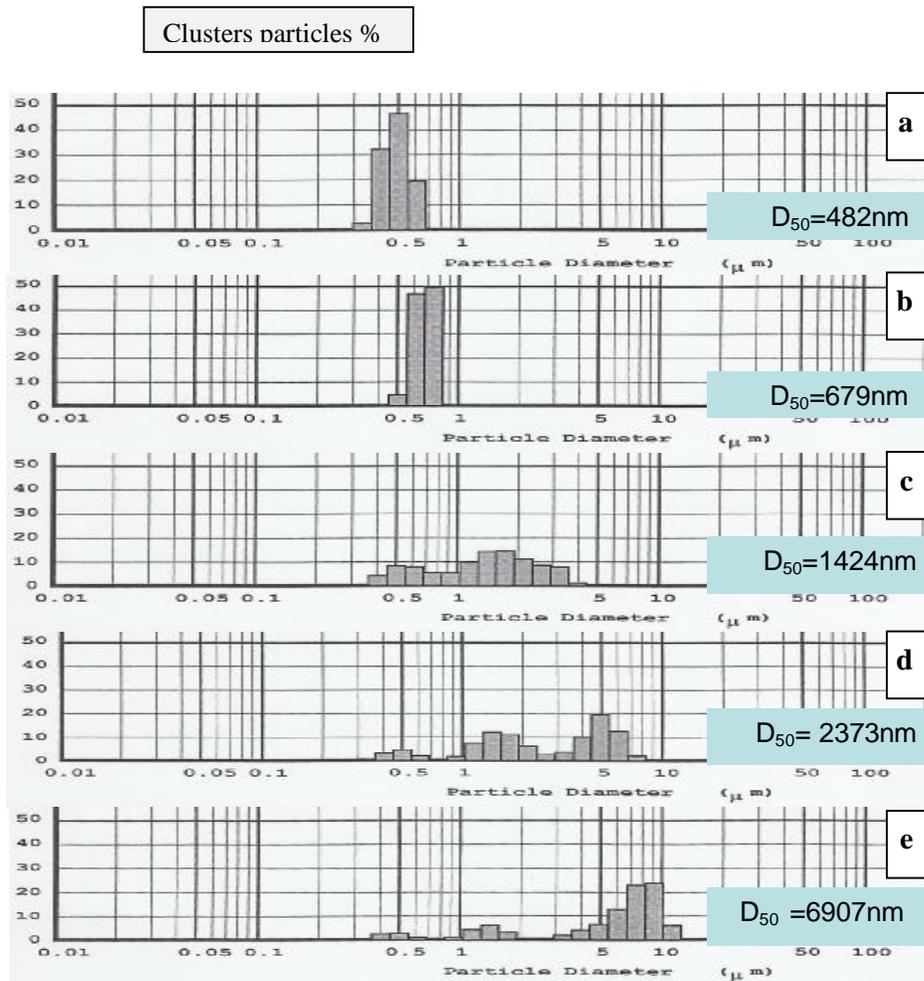


Figure (2) Variation of size distribution at D₅₀ nm for clusters Particles in the developed coating solution as a function of the xerogel heat treatment time at 220⁰C.



Figure(3) The results of measuring the size distribution for clusters particles in the developed coating solutions after varying the chemical composition of xerogel by partial removal of by-products constituents at different rates as follows : a- 10.2% b- 21.8% c- 42.1% d- 68.5% e- 80% .

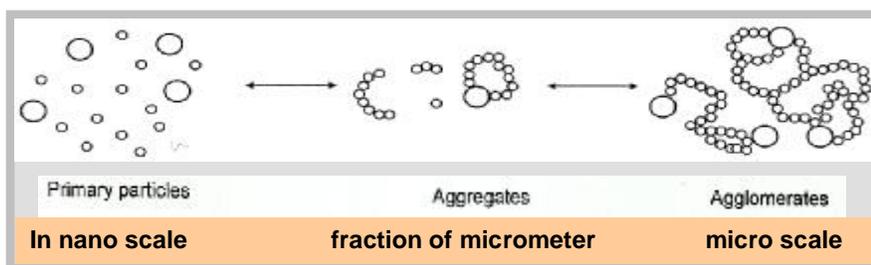


Figure (4) Mechanism of aggregation and agglomeration of the primary nano particles into clusters particles of micro size [19].

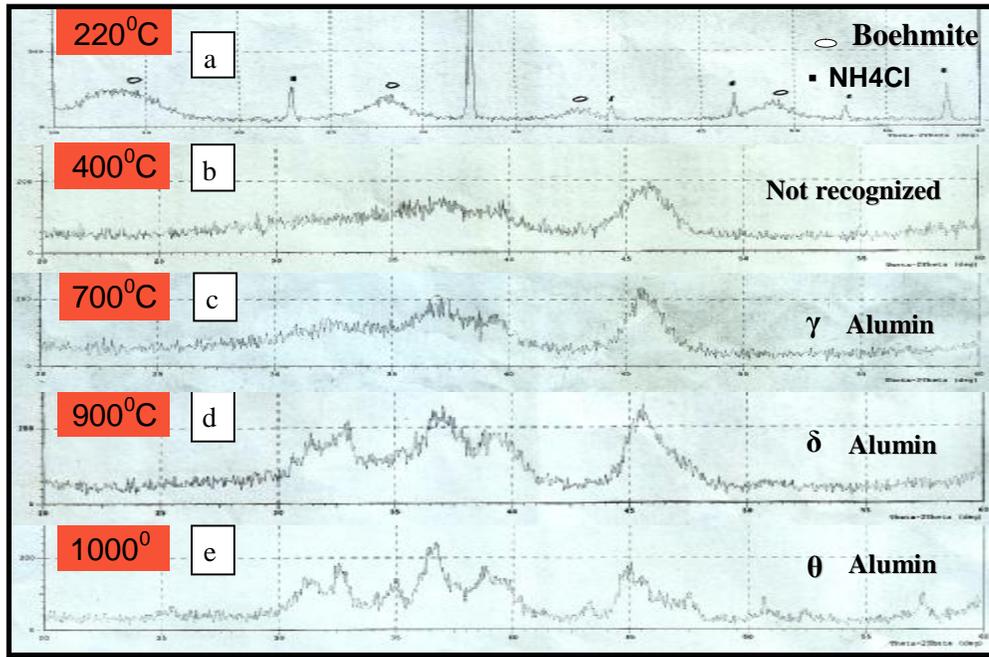


Figure (5) X-ray diffraction patterns curves for the xerogel granules at different heat treatment temperatures up to 1000°C showing the recognized phases.

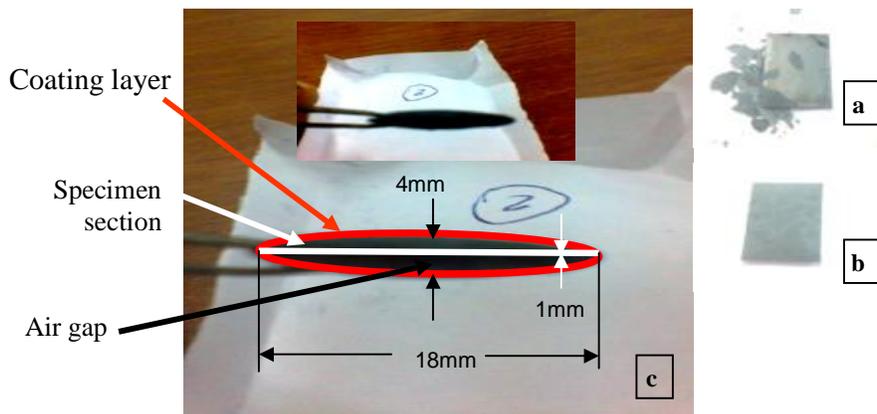
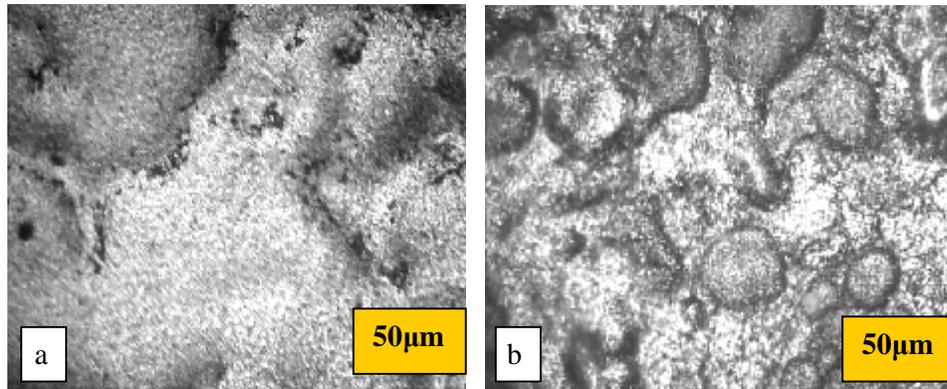


Figure (6) The results of the oxidation test at temperature 950°C for one hour.

- a- specimens coated with the conventional sol- gel showing fragments of spilled oxidescale.
- b- Specimens coated with the developed sol- gel.
- c- Section view of the specimen in (b) showing the extent of the cohesion and elasticity of the coating layer and how it deformed without showing cracks.



Figure(7) Qualitative properties of oxidation, a-the surface morphology of the conventional hybrid alumina coating layer after oxidation test for one hour at 950°C, b- rapid oxidation of specimen surface caused by loss of coating protection.

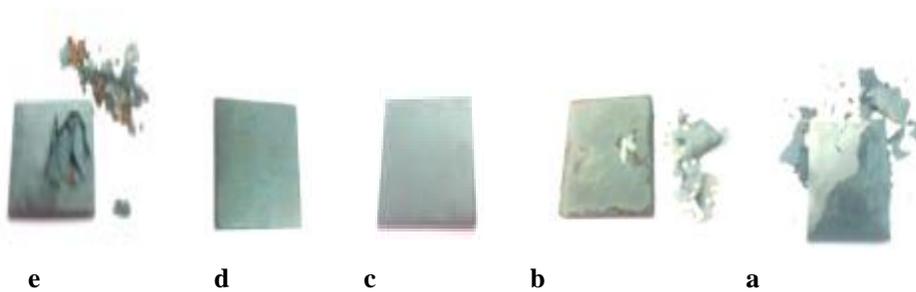


Figure (8) General views of coated specimens by different developed solutions, after oxidation test at 950°C, a- coating solution of $D_{50}=0.482\mu\text{m}$, b- $D_{50}=0.679\mu\text{m}$, c- $D_{50}=1.424\mu\text{m}$, d- $D_{50}=2.373\mu\text{m}$, e- $D_{50}=6.907\mu\text{m}$. (specimens a,b and e showing fragments of spilling oxide scale)

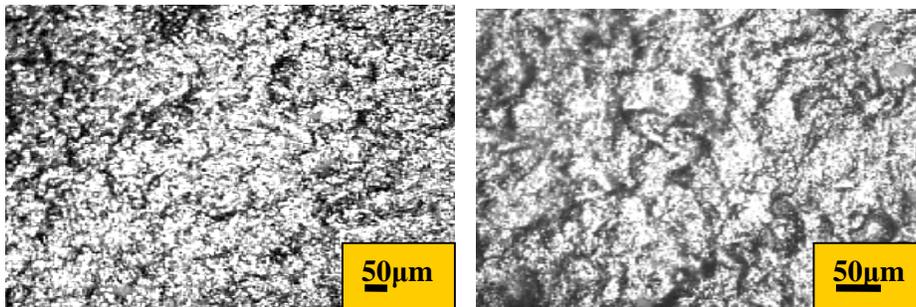


Figure (9) Developed coating surface morphology for the specimen (d) in figure(8), after oxidation test at 950°C.

Table (2) Calculation of oxidation rate reduction percent (OR %) at 950⁰C, for coated specimens by different developed coating solutions.

Particles size at D ₅₀ μm	Oxidation rate prior to coating S _{uncoated}	Oxidation rate after coating S _{coated}	R	OR%	$R = S_{coated} / S_{uncoated}$ $OR\% = 100(1 - R)$
0.482	42.1	25.84	0.613	38.7	
0.679		9.59	0.227	77.3	
1.424		5.05	0.119	88.1	
2.737		12.67	0.301	69.9	
6.907		23.36	0.554	44.6	

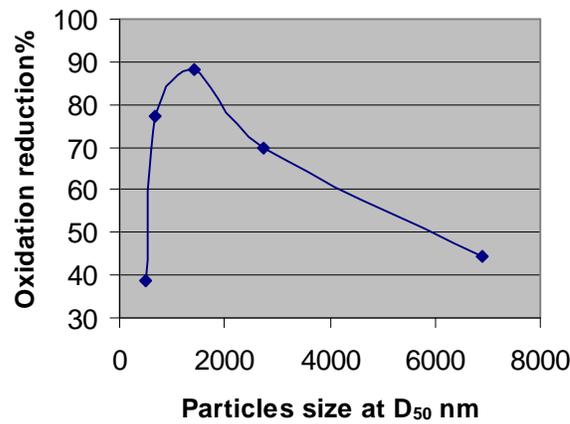


Figure (10) Oxidation reduction OR % in coated specimens by developed coating solution as a function of suspended Clusters Particles size in solution at D₅₀ nm.

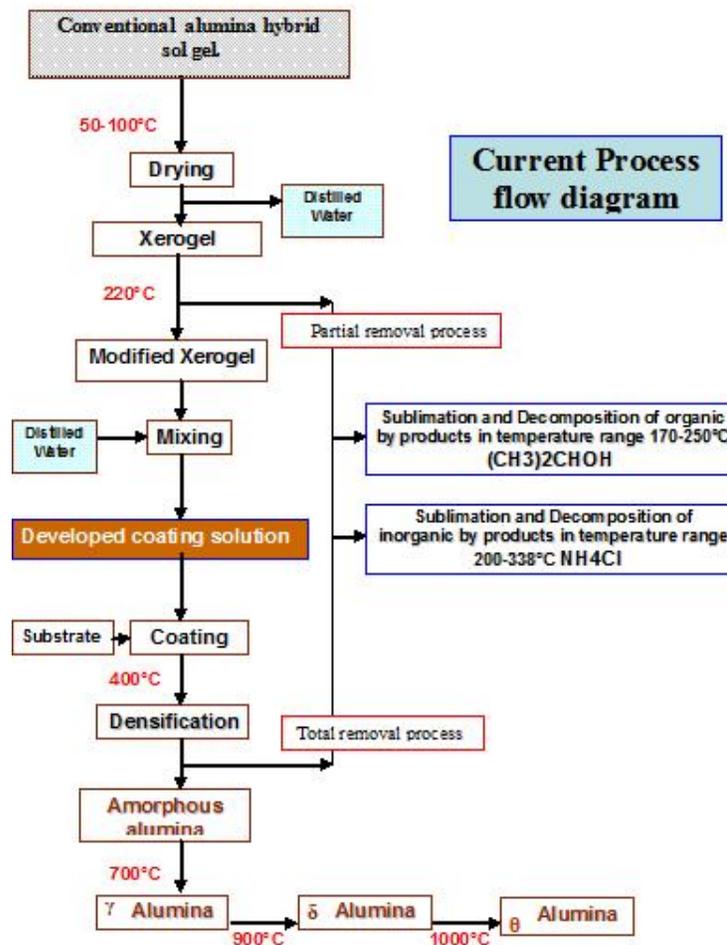


Figure (11) Process flow diagram for developing alumina coating solution for high temperature applications currently used in this worked.

CONCLUSIONS

1. Development of coating solution from xerogel of conventional hybrid sol gel after partial removal of associated unstable by-products up to 40-50% without using any additions is promising trend for high temperature coating applications. The development direction follow the mechanism of transfer the conventional hybrid sol gel a coating system of nano property to colloidal dispersion, then to micro suspension solution.
2. The results suggest that at certain average size of suspended particles in developed coating solution, the bulk of densification and the atomic diffusion process were

reduced, resulted in a considerable structural relaxation that seemed to minimize the distractive effects of residual stresses imposed by these processes, and stresses that build later by the progress of crystallization and the occurrence of four transition alumina phase changes which all together inducing cracks.

3. The developed coating solutions with prior conversion coating reduced the oxidation rate as compared with the steel before coating. The results shows that the maximum reduction in the rate of oxidation was 88% (8~9 times).

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