ALUMINIDE COATING BEHAVIOR OF AIS1330 STAINLESS STEEL[+]

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Abstract:

AISI330 stainless steel specimens, were coated by pack-cementation aluminization, using single step-high activity process at 1000° C ; for 3,5, and 7hours. The plain aluminide specimens were then heat-treated for 5, and 50 hours at 1000°C. The three types: uncoated, plain aluminide, and plain aluminide then heat treated specimens, were studied under cyclic oxidation at 1000°C for 240 hours in air. The results reveal that best results are obtained for 7 hours plain aluminide then heat treated for 50 hours specimen as compared to other specimens.

المستخلص:

تم طلاء عينات من الصلب المقاوم لصدأ AISI330 بالألمنيوم وبطريقة السمنتة لمرحلة واحدة وبفعالية عالية، عند درجة حرارة 1000 درجة مئوية ، ولمدة 3، 5، 7 ساعة. بعدها تم معالجة هذه العينات حرارياً عند 1000 درجة مئوية ولمدة 5 و 50 ساعة. تم دراسة عينات بدون طلاء ، عينات المنة، عينات المنة ثم معالجة حرارية تحت ظروف الاكسدة الدورية عند درجة حرارة 1000 درجة مئوية ولمدة 240 ساعة في الهواء. اظهرت نتائج هذه التجارب المقاومة الجيدة للاكسدة الدورية للعينات التي تم طلاؤها لمدة 7 ساعة ثم معالجتها حرارياً لمدة 50 ساعة مقارنة بالعينات الاخرى.

Introduction:

Stainless steels are a class of iron based alloys ; which are noted for their relatively high corrosion resistance .They contain 11-30% chromium ; in some cases with other additions notably nickel . Addition of chromium to iron will improve the resistance to corrosion and oxidation of iron ;by the formation of a relatively adherent passive oxide .So, stainless steels are used in a wide range of engineering applications ,such as petroleum industry ,furnace and boiler construction ,cement industry ,heat treatment shops etc .[1] .The severe environments encountered during operations will cause the oxide film to collapse due to the difference between thermal expansion coefficients of oxide film and base metal . So, a new oxide film will form , consuming more chromium . The chromium percentage is decreasing , and the oxide film becomes weaker [2] .Improving oxidation resistance of such steels , without changing

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component design becomes important , and it could be done by aluminum surface coating , which may be either diffusion coating or overlay coating [3].This paper presents the results of experiments used to ascertain the important variables which produce good oxidation resistance .

Backgrounds

Easy and cheap pack cementation is the common chemical vaporized deposition (CVD] process to produce diffusion aluminide coatings. In this process a part is immersed in a pack mixture which contains an aluminum source ,an inert filler usually aluminum oxide , and an activator such as ammonium chloride to accelerate aluminum transfer from the source to the substrate .The coating microstructure that results from the pack process depends on temperature of the pack ,the pack mixture , and any subsequent heat treatment [4 ,5] .

The coating microstructure that results from the pack process has been divided by Pint [6] into two types : those produced by high aluminum activity source and those produced by a low activity source . These are referred to aslow and high temperature types respectively. Fouquet [7], their work showed that only aluminum atoms are the only mobile species in aluminum deficient aluminides . Therefore high activity coatings grow primarily inward and low aluminum activity coatings grow outward . Also Levin et. al.[8], showed that high activity coatings consist mainly from the phase Ni_2Al_3 which is brittle ,hard , and has low melting point .The alloy cannot be used in practical work. So , heat treatment is necessary after aluminization process to transfer Ni_2Al_3 to NiAl phase which is ductile , less hard , and has a higher melting point. Al-Hashimee [9], showed that for short time heat treatment, diffusion of aluminum inward is greater than diffusion of nickel outward. But increasing either time or temperature of heat treatment , increase nickel diffusion rate outward forming the stable NiAl phase . Degradation of stainless steels is due to the reaction between alloy surface and the surrounded atmosphere, leading to oxidation of chromium. Chromium percentage will decrease continuously the surface scaling and forming of the oxide film .Bacos et. al.[10], research shows that chromium oxide oxidation growth rate is 5*10 EXP-12 gm^2 cm-4 s-1 at 1000^oC and can remove about 5µm chromium after 100 hrs oxidation period. On the other hand aluminum oxide has an oxidation growth rate of (10^-13)gm^2/cm4.s1 and can remove only 5µm of coating layer during 400hrs. Clarck et. al.[11]&Nicolls et. al.[12], gave the explanation for the failure of oxide film .The formation of oxide film lead to the formation of voids at oxide-coating layer interface by transformation of aluminum and chromium atoms into oxide film .The voids will grow in volume by continuous oxidation process to form a large vacancy which leads to separation from the surface and forming a scale . Also oxidation film growth form large stresses by making the oxide film under compressive stress and coating surface under tensile stress. The oxide film and coating surface have different thermal expansion coefficient, leading to the formation of thermal stresses causing breaking of oxidation layer.

Experimental Side:

1-Specimen Preparation for Coating Process:

AISI330 stainless steel specimens have the following chemical composition as were received from Austria Campingspor Ges.m.b.H., as shown in Table (1) .

Table (1) chemical composition of st. st. AISI330

C%	Si%	Cr%	Ni%	Hardness
0.12	1.3	15.8	35	223HV

Specimens were cut by Metaserve cut off machine to 20x20x2mm. Then the specimens were ground by grinding paper with grit: 220, 320, 600, and 1000.

2-Aluminide Coating:

Aluminization process was carried out using aluminization mixture which contained 47.5% wt aluminum, 1.0% wt ammonium chloride, 51.5% wt aluminum oxide Aluminization was carried out by high activity process at 1000^0C for 3, 5,and 7 hrs, by inserting the stainless steel specimen and aluminzation mixture inside an alumina tube with dimensions 100mm long and 35mm diameter. The two ends of the alumina tube were closed firmly by fire clay. Aluminizatio process was carried out using tube furnace Hereaus RS-80.

3-Heat Treatment:

Aluminide specimens were heat treated by heating to 1000 ̊C for 5 and 50 hrs(short time and long time heat treatment respectively) using Heraeus RS-70 electric furnace.

4-Oxidation:

Oxidation was done by thermal cycling in air to study specimens behavior against oxidation process. Oxidation process was done by heating to 1000^oC for 24 hrs thermal cycle. The specimens were cooled to room temperature, then reheated to 1000^oC for 24 hrs. The specimens before oxidation were cleaned Scogell TG51 Ultrasonic bath with 5%Sodium Hydroxide solution was used. Then the samples were dried and weighed by
0.1mg Sartorius electric balance.

5-Microscopic Examination:

Aluminide, heat treated, and oxided specimens were mounted using Metaserv mounting press .Grinding and polishing were carried out by the following process.

Grinding Process:

Using Silicon Carbide grinding paper with grit :220, 320 600,1000,and 1200,each grit for 1 minute .

Polishing Process:

Using 6µm Alumina suspension for 2 minutes, and 3µm alumina suspension for 3 minutes. The specimens were then etched by heating them in water bath at 40^oC. The etchant used contains [13]:1 part Nitric Acid, 2 parts Hydrochloric Acid, 1 part Hydrogen Peroxide , 2 parts Glycerol
Micrographs were taken using Panasonic DMC-LC33 Digital Camera .

6-Microhardness:

Using Wolpert V-Tester 2, Vickers microhardness for aluminide, heat treated, and oxided specimens was measured with 0.2 Kgf applied load .

7- x-ray Diffraction :

Philips x-ray Diffractor was used to reveal the various phases that were formed on specimen surface after aluminization ,heat treating , and oxidation .

Discussion

1-Aluminization Process

As mentioned before , AISI 330 stainless steel specimens , were coated by high activity aluminization process at 1000^0C . Hence , aluminide coating layer was formed by inward aluminum diffusion.The relationship between intake weight of aluminum, and average aluminide coating thickness , with aluminization time is parabolic as shown in Figs.1&2 and micrographs in Fig.3,4,5 . Ficks law is obeyed , so diffusion of aluminum into specimen surface is the main process for coating layer . And these results agree with [9],while x-ray diffraction results for aluminide specimens showed that the phases which formed were mainly NiAl , $NiAl_3$,and Ni_2Al_3 . For three hour aluminization time specimens , $NiAl_3$ was the major phase formed . This can be explained by insufficient time of for aluminum to diffuse inward the substrate. So, average coating thickness was 29 µm. . When aluminization time was increascd to 5 and 7 hrs , average coating thickness increased to 47 and 56 µm respectively . Also , phases formed were Ni_2Al_3 and NiAl as were revealed by x-ray diffraction , but with increase in NiAl phase percentage as aluminization time increased . Ni_2Al_3 is a brittle , hard ,and unstable phase , and would transform to less hard and stable NiAl phase [11] .Microhardness across aluminide coating layer is shown in Fig (6) . Maximum microhardness value is HV521 measured at 15µm from edge of coating layer for 3hrs aluminization time specimen , while the value decreased to HV495 at 25µm from the coating edge for 5hrs aluminization time specimen , and HV475 at 30µm from the coating edge for 7hrs aluminization time specimen . This is congruent with results discussed previously i.e. transformation of hard Ni_2Al_3 phase to a less hard NiAl phase by inward aluminum diffusion with increasing aluminization time.

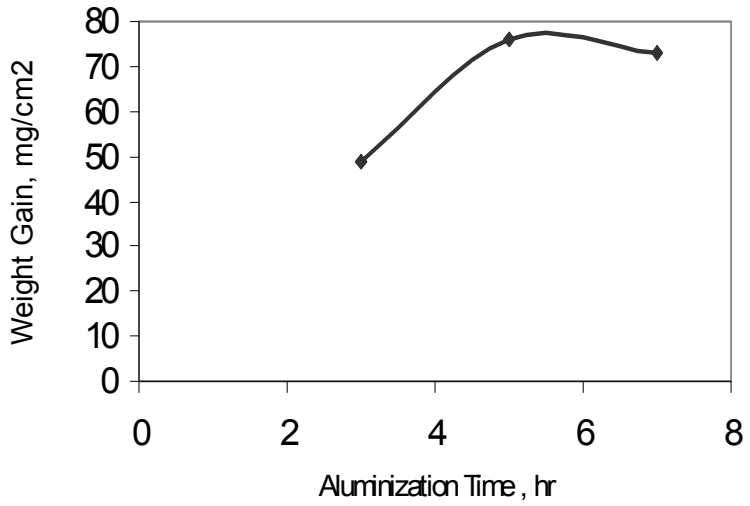
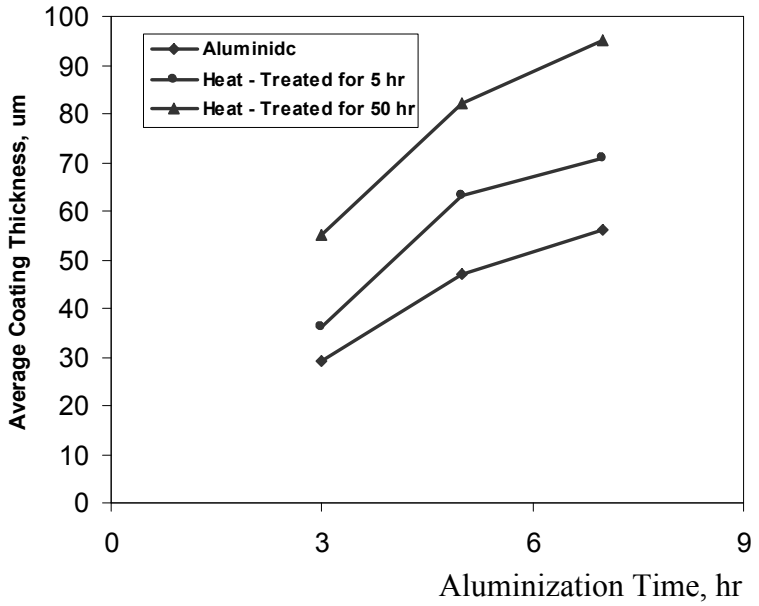


Fig (1) Relationship between Aluminization Time and Weight Gain for St.St AISI330 Specimens



Fig(2) Relationship between Aluminization Time and Coating Thickness for St.St AISI330 Specimens

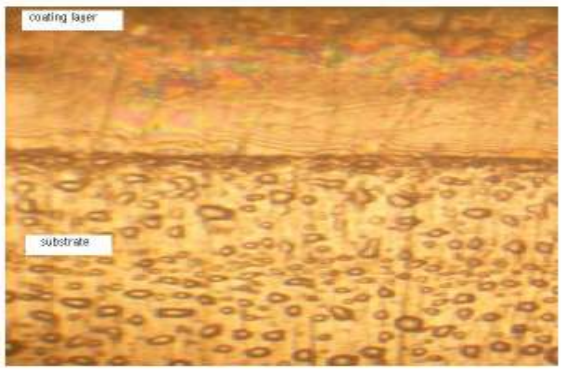


Fig (3) 3hrs Aluminide Coating at 1000 ℃ for St.St AISI330 Specimens at x400

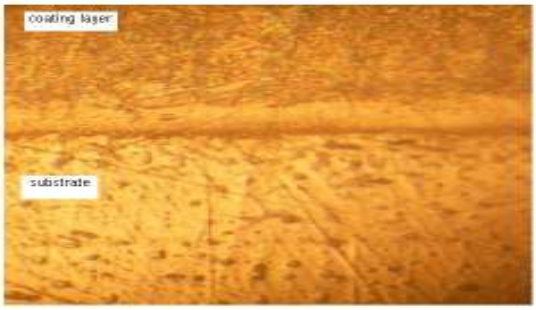


Fig (4) 5hrs Aluminide Coating at 1000 ℃ for St.St AISI330 Specimens at x400

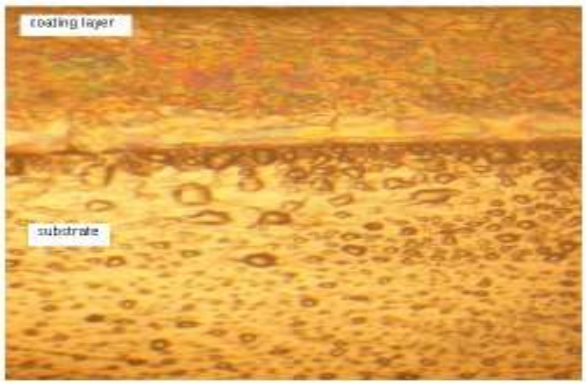


Fig (5) 7hrs Aluminide Coating at 1000 ℃ for St.St AISI330 Specimens at x400

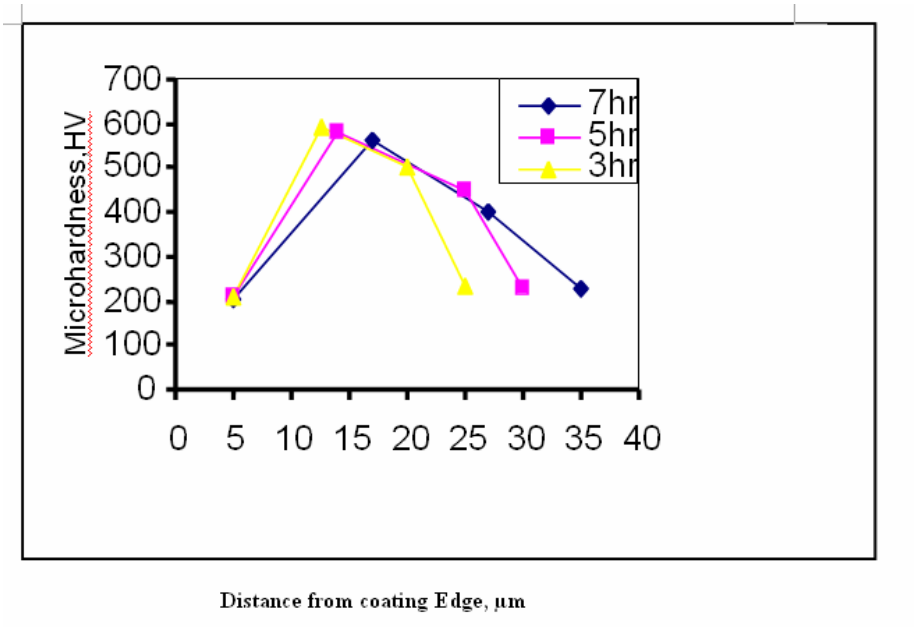


Fig (6) Microhardness of Coating Layer after Aluminization Process

2- Heat Treatment of the Aluminide Specimen:

After aluminization process, the aluminide coating layer is unstable due to the formation of Ni_2Al_3 phase , which will continuously transform to a stable structure with time . So , the aluminide specimens were reheated to 1000^0C in an evacuated atmosphere for 5 and 50 hrs .Figs (7-12) show the microstructure of the aluminide coated specimens after heat treating .

For 5 hrs heat treated specimens , x-ray diffraction revealed that the phases formed were : Al_2O_3 , NiAl , and Ni_2Al_3 . Aluminum Oxide (Al_2O_3) appeared as traces on coating layer surface . But Ni_2Al_3 percentage decreased by transforming into NiAl phase, due to mutual diffusion of nickel and aluminum. Aluminum diffused inward , while nickel diffused outward .Thus, the average coating thickness layer increased from 56 to 71µm for 7 hrs alumization time specimen , while maximum microhardness value decreased from 475 HV to 470 HV as shown in Fig(13).

When heat treating the specimens for 50 hrs , x-ray diffraction results for 7 hrs aluminization time specimen revealed formation of the phases :NiAl , Ni_3Al , Al_2O_3 , FeCr , and Al_5Cr . Compared with 5 hrs heat treated specimens, the unstable Ni_2Al_3 phase had completely transformed to the stable NiAl phase. Formation of Ni_3Al phase can be explained by greater nickel diffusion rate than that of aluminum [8]. Also , Al_2O_3 was found as traces in the specimen coated layer . And due to the partial solubility of specimen alloying constituents in aluminum, FeCr, Al_5Cr, and Carbides were formed as particles on boundary layer between coating layer and substrate [7] . Also, due to diffusion of both nickel and aluminum, coating layer got thicker(95µm). Formation of stable NiAl phase leads to decrease in microhardness value to a practical and moderate value of 432 HV. Hence the specimen is ready for practical use. [6]

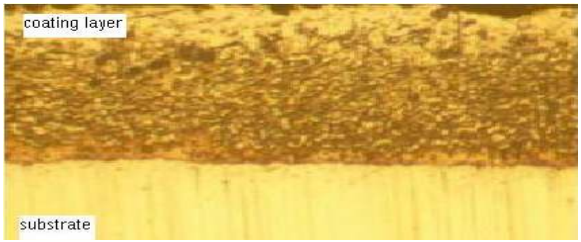


Fig (7) 3hr Aluminide Coating at 1000 ℃, 5 hrs Heat Treatment at 1000 ℃ for St.St AISI330 Specimens at x150

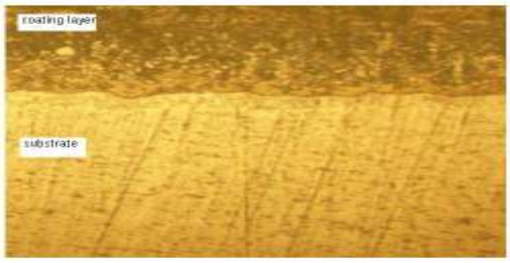


Fig (8) 5hr Aluminide Coating at 1000 ℃, 5 hrs Heat Treatment at 1000 ℃ for St.St AISI330 Specimens at x150

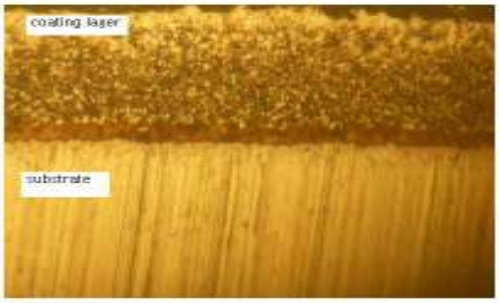


Fig (9) 7hr Aluminide Coating at 1000 ℃, 5 hrs Heat Treatment at 1000 ℃ for St.St AISI330 Specimens at x150

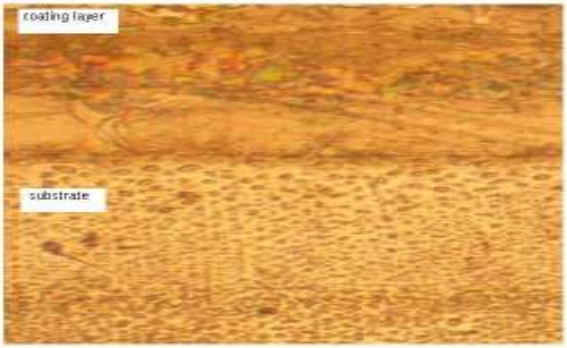


Fig (10) 3hr Aluminide Coating at 1000 ℃, 50 hrs Heat Treatment at 1000 ℃ for AISI330 St.St. Specimens

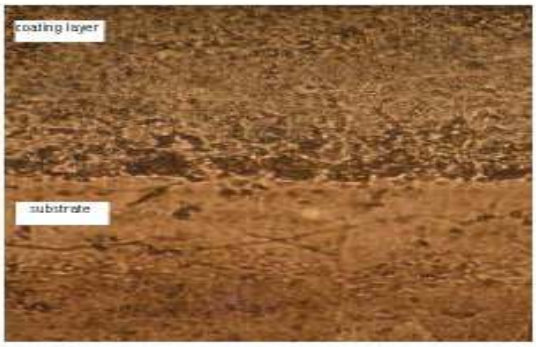


Fig (11) 5hrAluminide Coating at 1000 ℃, 50 hrs Heat Treatment at 1000 ℃ for AISI330 St.St. Specimens

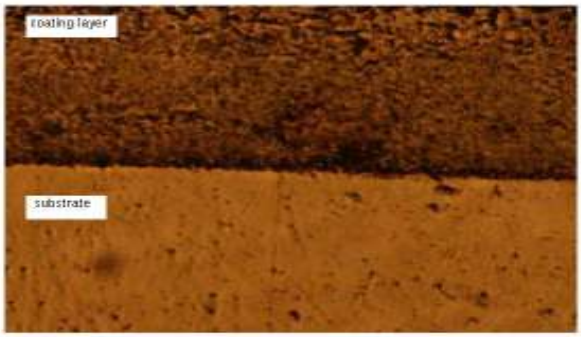


Fig (12) 7hr Aluminide Coating at 1000 ℃, 50 hrs Heat Treatment at 1000 ℃ for AISI330 St.St. Specimens

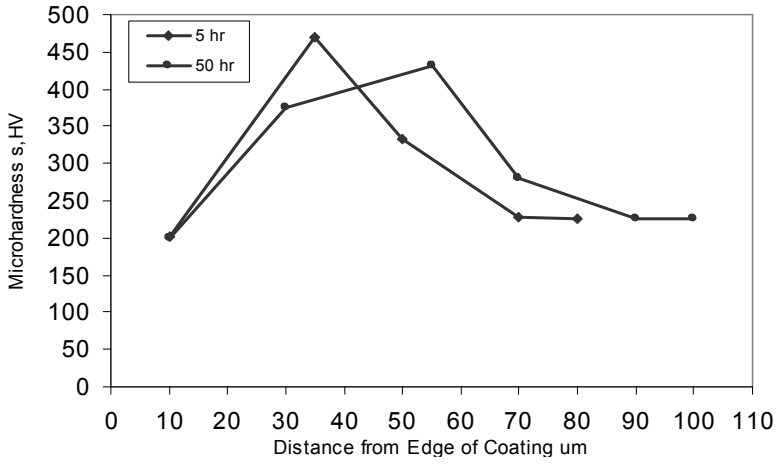


Fig (13) Microhardness of Coating Layer after Aluminization Process for 7 hrs, then Heat Treating at 1000 ℃

3-Oxidation Performance:

Figs.(14, 15, 16,17) represent the oxidation behavior during cyclic oxidation for uncoated AISI330 stainless steel specimen, aluminide specimen for 7 hrs, then 7hrs aluminide and heat treated for 5 hr specimens, and aluminide specimen for 7 hrs then heat treated for 50 hrs respectively .

Oxidation of uncoated specimen led to formation of Chromium Oxide Cr_2O_3 by diffusion of chromium towards the oxide film., leading to decrease in chromium concentration at oxide film – specimen surface interlayer. Hence ,the unstable oxide $FeCr_2O_4$ would form , allowing iron ions to move to specimen surface forming Fe_2O_3 [11] . Thermal stresses caused the difference between thermal expansion coefficients of oxide film and the substrate . The oxide film would collapse as scale Fig(18). The specimen decreased in weight 511mg /cm^2 after tenth oxidation cycle Fig (14) .

Oxidation of 7 hr aluminide specimens , an aluminum oxide film would form on specimen surface . This oxide film is dense , non-porous and well adhered to specimen surface , so preventing oxygen gas from diffusing into specimen surface . Chromium oxide had also formed , which would dissolve in aluminum oxide whenever being heated over 900^oC [9] . But the aluminum oxide film may fail due to:

1- diffusion of aluminum inwards, and diffusion of specimen alloying constituents outward.

2- reaction with surrounding atmosphere . Thermal stresses may cause breakage of this film as scale . The new surface will oxidize , and the specimen will lose some of its weight [10] . From Fig(16), aluminide coating layer offered prevention from oxidation 200 hrs for specimen aluminide for 7 hrs. Prevention from oxidation was raised to 230 hrs by heat treating the previous specimen for 5 hrs. Best prevention from oxidation was achieved by heat treatment of the specimen for 50 hrs Fig(17). This can be explained by increase in nickel percentage at specimen surface, due to the formation of NiAl , as shown before . So, nickel will oxidize to NiO as a tiny film, raising adherence of oxide film to the specimen surface , giving better protection during practical work .[3]

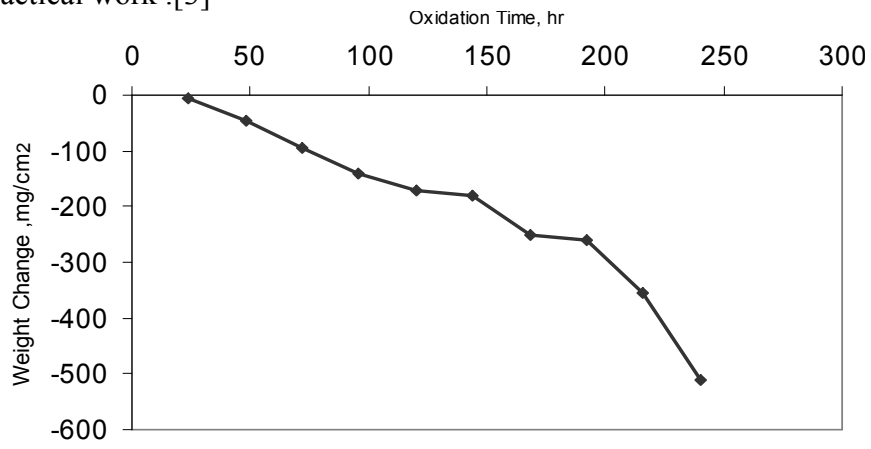


Fig (14) Cyclic Oxidation of Uncoated St.St AISI330 Specimens

Fig (15) Cyclic Oxidation of 7hrs Plain Aluminide St.St AISI330 Specimens

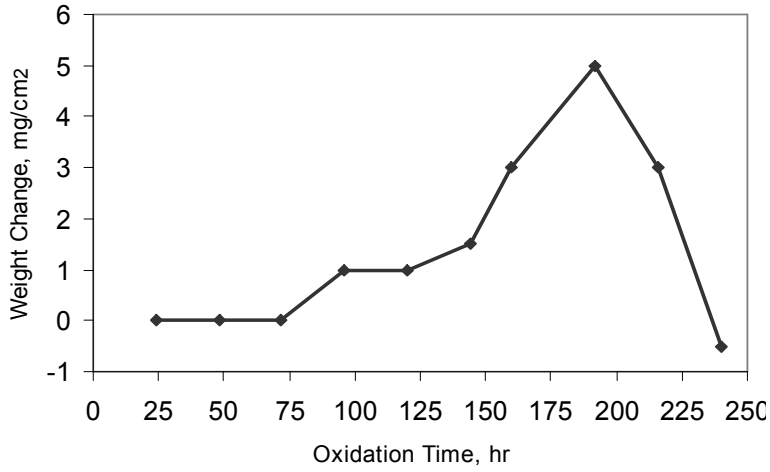


Fig (16) Cyclic Oxidation of 7 hr Aluminization then Heat Treated for 5 hrs at 1000 ℃ for St.St AISI330 Specimens

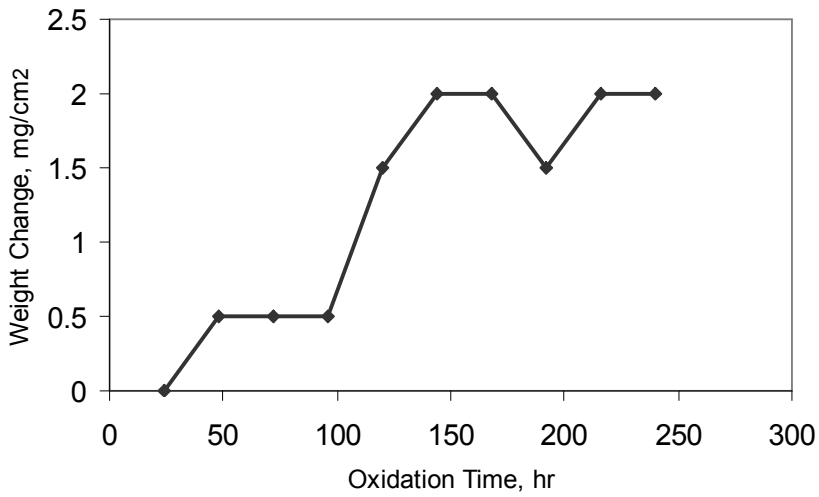


Fig (17) Cyclic Oxidation of 7 hr Aluminization Time, then Heat Treated for 50 hrs at 1000 ℃ for St.St AISI330 Specimens

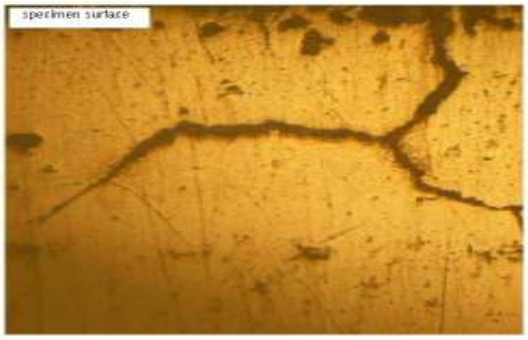


Fig (18) Oxidation of Uncoated St.St AISI330 Specimens at x200

Conclusions

1- Aluminide coating thickness increases with increasein aluminization time, according to parabolic relationship, which proves that coating process is achieved by diffusion.
2- Hard, unstable Ni_2Al_3 phase is the major phase formed in the aluminide coating layer, which transformed completely, after long time heat treating, to stable-less hard NiAl phase.
3- Good oxidation resistance is achieved for the plain aluminide for 7hr, 50hr heat treated specimen, as compared to other specimens.

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