Eng.&Tech.,Vol.26,No.6,2008

Oxidation Properties of Steel-T22 Alloy Coated by Simultaneous Ge-Doped Chromizing-Siliconizing Process

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Received on:21/10/2007
Accepted on: 7/1/2008

Abstract

Diffusion coating was carried out at 1050 ^oC for 6 h under argon atmosphere by simultaneous Ge-doped chromizing-siliconizing process on low alloy steel type-T22. Cyclic oxidation tests were conducted for the uncoated and for the chromizing – Siliconizing coated steel-T22 alloy at 800 ^oC . For the Ge-dopded chromizing-siliconizing coated steel, the cyclic oxidation was carried out in the temperature range 600-800 ^oC in air for 100 h at 5 h cycle. The results showed that the oxidation kinetics for uncoated steel-T22 alloy in air at 800 ^oC follow a breakaway oxidation and the phases present are FeO (Wustite), Fe_3O_4 (Magnetite) and Fe_2O_3 (Haematite).

The oxidation kinetics for chromizing –Siliconizing coated system in air at 800 ^oC was found to be parabolic. Oxide phases that formed on coated system are SiO_2 and Cr_2O_3. The oxidation kinetics Ge-doped chromizing –Siliconizing coated system in air in the temperature range 600-800 ^oC was found to be parabolic .Oxide phases that formed on coated system are SiO_2 and Cr_2O_3. The Ge addition improves the oxidation resistance of low alloy steel.

Keywords: Steel-T22, Cyclic oxidation, Chromizing-Siliconizing, Pack cementation

الخلاصة

في هذا البحث تم اجراء الطلاء الانتشاري في درجة حرارة $1050\ ^oC$ ولمدة 6 ساعة في جو من غاز الاركون باستخدام نظام الجرمانيوم –الكروم –السليكون لسبيكة الفولاذ المنخفض السبائكية نوع T22 . اجريت اختبارات الاكسدة بشكل دوري (Cyclic Oxidation) على سبيكة الفولاذ المنخفض السبائكية نوع T22 وانظمة الطلاء النوع الاول سبيكة الفولاذ المنخفض السبائكية نوع T22 / سليكون- كروم (chromizing –Siliconizing) ونظام الطلاء النوع الثاني سبيكة الفولاذ المنخفض السبائكية T22 / سليكون- كروم – جرمانيوم .– (Ge-doped chromizing Siliconizing) في الهواء بدرجة حرارة ^oC 600-800 لمدة 100 ساعة بمعدل 5 ساعة للدوره الواحدة.

اظهرت النتائج ان سلوك التاكسد لنظام سبيكة الفولاذ المنخفض السبائكية نوع T22 بدون طلاء يتبع التاكسد الانفصالي (breakaway oxidation) وان الاطوار المتكونة هي :

FeO, Fe_3O_4 and Fe_2O_3.

ان سلوك التاكسد لنظام النوع الاول سبيكة الفولاذ المنخفض السبائكية نوع T22 / سليكون- كروم (chromizing –Siliconizing) ونظام الطلاء النوع الثاني سبيكة الفولاذ المنخفض السبائكية T22 / سليكون- كروم – جرمانيوم . (Ge-doped chromizing –Siliconizing) هو قطع المكافيء في درجة حرارة ^oC 800 -600 في الهواء وان الاطوار المتكونه هيSiO_2 and Cr_2O_3 .

ان اضافة الجرمانيوم يؤدي الى تحسين سلوك التاكسد لسبيكة الفولاذ المنخفض السبائكية T22 .

Introduction

Low alloy steels are generally considered to comprise plain carbon steels and steels with a total alloying content of up to 12%. These materials are not generally selected for resistance to high temperature corrosion but, they are often required to operate in high temperature aggressive environments [1]. Low alloy steels have been used at many industrial plants, their corrosion resistance needs to be improved by

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https://doi.org/10.30684/ etj.29.6.11
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surface modifications [2- 4]. Among the various surface- modication methods, pack cementation has been applied for many years to enrich the alloy surfaces with chromium or aluminum. Simultaneous deposition of two elements by pack cementation is very effective in protecting substrates from hot corrosion and oxidizing environments at high temperature [5-7].

Of all the alloying elements added to steels, Cr has been the most used for improving the corrosion properties. In terms of high temperature oxidation, steel containing approximately 10%Cr are capable of forming a continuous, highly protective film of Cr2O3 [1]. Rahmel and Tobolski [8] found that the addition of up to 4%Si to Fe, exposed to pure oxygen, O2 + H2O or CO2 in the temperature range 750-1050 ^{o}C, give a limiting corrosion rate due to the formation of an iron-silicate layer. Adachi and Meier [9] studied the oxidation of Fe-Si alloys under isothermal and cyclic oxidation conditions, in air, between 900 ^{o}C and 1100 ^{o}C . They found that the oxidation rate decreased with silicon content, such that at 10wt% the oxidation rate was lower than that conferred by Cr, due to the formation of a continuous film of SiO2. For Fe-Si, then, 2.5-3%Si is required for healing layer formation, irrespective of the temperature. For Fe-Cr-Si, however, the critical Si content decrease with increasing Cr content and temperature.

Chromizing process is a method for developing a surface coating providing hardness, wear and corrosion resistance [10]. Currently, chromized coatings are used for the corrosion resistance of turbine blades, for boilers and other petrochemical applications [11]. Halide-activated pack cementation improves the corrosion resistance of steel greatly by co-depositing Cr and Si on the surface of steel. Harper et al. [12] studied the co-deposition of Cr with Si or Al on plain-carbon steels and low-alloy steels. Wan et al. [13-14] have co-deposited Cr- Si on medium-carbon steel, ultra-high strength steel and stainless steel by using elemental Cr and Si powders instead of master-alloys of Cr and Si.

Wei et al.[15] studied the co-deposition of Cr-Si into Cr17Ni2 stainless steel similar to AISI 431 using a pack cementation process. They showed that the thermal treatment of the coating resulted in a reduction of tensile strength, but the improvement of impact toughness, although the coating had little effect on the mechanical properties of the bulk.

The aim of this work is to find a new technique to deposit Ge-doped Cr and Si (Ge-doped chromized/siliconized) simultaneously by pack cementation using a single-step process on low alloy steel (type T22 used as superheater in boilers). Also the codeposition of Cr and Si (chromizing – siliconizing) will be investigated. This single step process is an economical technique for codeposition of two elements, which will reduce the use of materials, labor, time and energy. In addition, The cyclic oxidation behavior of uncoated low alloy steel , chromized/siliconized low alloy steel and Ge-doped chromized/siliconized diffusion coating will be studied in the temperature range (600-800 $^{\circ}$C) in air .

Experimental Work

The substrate used in this study was low alloy steel (Type T_{22}-ASTM). The nominal composition of low alloy steel is shown in Table 1. The spectrochemical analysis is shown in Table 2.

The low alloy steel samples were cut into squares shapes with dimensions (20mm× 20×mm×5mm) . Small hole of 2 mm diameter was drilled in each sample for holding. All surfaces, including the edges were wet ground using 120, 220, 320, 600, 800, and 1200 grit silicon carbide papers. These samples were then cleaned with water, degreased with acetone and then ultrasonically cleaned for 30 minutes using ethanol as a medium. After drying, the samples were stored in polyethylene zip-lock bags.

The samples dimensions were measured using a calibrated micrometer with a precision ± 0.01 mm and then the surface area of each sample was calculated. The weight of each sample was measured using a Mettler digital microbalance (Switzerland) with an accuracy of ± 0.1 mg.

Many experimental works were carried out to investigate the feasibility of simultaneous chromizing - siliconizing and simultaneous chromizing - siliconizing – germanium (This is called Ge-doped chromizing - siliconizing) of low alloy steel (T_{22}) by pack cementation process. A series of further experiments were performed to investigate the effects of pack composition, deposition temperature and time on the kinetics of coating growth process.

The pack mixture used for chromium-silicon diffusion coating consists of 16 wt.%Cr powder (50-150 m in particle size) as a chromium source, 6 wt.%Si powder (38-170 m in particle size) as a silicon source, 2Wt.% NaF and 2Wt.%NaCl as activator and the balance was silica-powder (70-120 m in particle size). All pack powders was sized by sieving method. The pack powder was mixed in a ball-mill (type 05-102, Fritsch Pulaeristte-Germany) at 300 r.p.m for 180 min. with addition of n-hexane (n-C_6H_{14}) in order to prevent powders oxidation due to frictional heat (balls and liners made of porcelain material to prevent pack contamination). Follow Won et al. [2] procedure, the pack was then dried at 75°C for 15 min. The pack mixtures used for chromizing - siliconizing and for Ge-doped chromizing –siliconizing are shown in Table 3.

Low alloy steel (type T_{22}-ASTM) was placed in a sealed stainless steel cylindrical retort (inner retort) in contact with the pack mixture. The inner retort was then put in another stainless steel cylindrical retort (outer retort). The outer retort has two tubes one for argon gas inlet and the other for argon gas outlet. Type-K calibrated thermocouple was inserted through the cover of the outer retort for recording real temperature near the inner retort. Pack Cementation process was carried at 1050 °C for 8 hrs under argon atmosphere. It was found that diffusion coating time of six hour at 1050°C produces coating thickness of 65-80 m. X-ray diffraction (XRD) and energy dispersive X-ray fluorescence (EDXRF) were used to characterize the resulting coating structures and compositions. The cross section was etched for approximately 10 seconds in an etchant (3parts hydrochloric acid, 2 parts nitric acid, 2 parts acetic acid, and 1 part glycerol by volume according) [16].

The uncoated and the coated low alloy steel (chromium-silicon diffusion coating, and Ge-doped chromium-silicon diffusion coating samples) were accurately weighed. Cyclic oxidation tests were carried out in a programmable furnace (manufactured by Sheffiield, England) in the temperature range 600-800 °C in air at 1 atmospheric pressure for Ge-doped chromium-silicon diffusion coated. For uncoated low alloy steel and for chromium-silicon diffusion coated low alloy steel the cyclic oxidation tests were carried out in at 800 °C in air at 1 atmospheric pressure. Each heating cycle is 5 hrs at the test temperature and cooling in still air. The samples were removed from the furnace, allowed to cool, ultrasonically cleaned in ethanol to detach the spalled oxide and the weight change per unit surface area was determined.

Results And Discussions

Present work attempted to determine the effect of chromizing –siliconizing and Ge-doped chromizing –siliconizing diffusion coating on oxidation behavior of low alloy steel type-T_{22} in air. The cross section of uncoated low alloy steel type-T_{22} and the chromizing-siliconizing low alloy steel after cyclic oxidation in air at 800 ^{o}C for 100 hrs at 5 hrs cycle are shown in Figure 1. The microstructures revealed a large number of voids that exist at the scale /alloy interface and in the alloy during the cyclic oxidation of uncoated low alloy steel type-T_{22} after cyclic oxidation at 800 ^{o}C . These voids reduce the scale/ alloy contact and hence facilitate spalling and then breakaway oxidation. These voids may act as concentration sites of thermal stresses induced during heating and cooling leading to crack formation and spalling of the surface scale. X-ray diffraction analysis (XRD) showed the phases present on the scale formed on uncoated low alloy steel type-T_{22} in air after 100 hr at 10 cycle at temperatures range 800 ^{o}C are : FeO (Wustite), Fe_3O_4 (Magnetite) and Fe_2O_3 (Hematite). These results are in good agreement with the work of Abass [17] and Shier [1].

For chromizing- siliconizing low alloy steel Figure 1, the cross section is so dense reveals and no voids were observed at the scale /alloy interface and in the alloy during the cyclic oxidation at 800 ^{o}C . An interdiffusion zone was found at the scale /alloy interphase. X-ray diffraction analysis (XRD) showed the phases present are SiO2, and Cr2O3.

The cross section for Ge doped chromizing- siliconizing low alloy steel is so dense and no voids were observed at the scale /alloy interface and in the alloy during the cyclic oxidation in air at 600- 800 ^{o}C as shown in Figure 2. Grain growth was enhanced by Ge addition and the interdiffusion zone becomes smaller. X-ray diffraction analysis (XRD) showed that the phase present at the coated surface consist mainly from CrSi2 while germanium or germanium compounds phases that probably exists in the outer layer in insufficient amount are undetectable by the X- ray diffraction analysis because of the lower germanium content in the coated layer. The phases present on the Ge doped chromizing- siliconizing low alloy steel oxidized at 600-800 ^{o}C are SiO2 and Cr2O3 as shown in Figure 3.

The specific weight gain is plotted vs. oxidation time at 800 ^{o}C during cyclic oxidation in air for uncoated low alloy steel type-T_{22} , for the coated systems chromizing-siliconizing, and for Ge-doped chromizing-siliconizing as shown in Figure 4. The uncoated low alloy steel exhibit three types of behavior when oxidized in air: protective, transitional and linear-breakaway. The time required to breakaway and the breakaway rate being of crucial importance in determining component life.

The oxidation behaviors of the coated systems chromizing-siliconizing and Ge-doped chromizing - siliconizing at 800 ^{o}C are parabolic. It is clear the addition of germanium increases the oxidation resistant of low alloy steel.

The results of cyclic oxidation experiments conducted at 600-800 ^{o}C in air for Ge-doped chromizing - siliconizing coated low alloy steel for 100 hrs at 5 hrs cycle are presented in Figure 5. No spalling was observed during cyclic oxidation . These data were fitted to the equation [$(\Delta W/A) = K t^{n}$]. Where ΔW is the weight change (mg/cm^2) , A is the sample surface area (cm^2) , K is the rate constant ($mg/ cm^2 \sqrt{hr}$) , n is the growth- rate time constant, and **t** is the time of oxidation(hrs). The exponential constant n characterizes the oxidation rate as follows: if n = 1, the oxidation rate is linear, n = 0.5 the oxidation rate is theoretically parabolic, if n = 0.33, then the oxidation rate is cubic [18]. The result showed that for Ge-doped chromizing -siliconizing coated low alloy steel oxidized in air at 600-800 ^{o}C, the value of n is about 0.5 which indicates the oxidation kinetics is parabolic. Furthermore, the specific weight gain was then plotted vs. the square root of oxidation time which gives a linear relationship as shown in Figure 6. The slop is again equal to the rate constant K (mg/ cm^2 √**hr).** To calculate the parabolic rate constant K_p (gm^2/ cm^4 **sec**), the following conversion factor was used.

K^2 (mg/ cm^2 √**hr)**^{2} / 360000 = K_p (gm^2/ cm^4 **sec**).

The values of K_p and n are listed in Table 4 . For Ge-doped chromizing -siliconizing coated low alloy steel oxidized in air at 600-800 ^{o}C. At 800 ^{o}C the parabolic rate constants for chromizing -siliconizing coated low alloy steel is about four times the K_p value for Ge-doped chromizing -siliconizing coated low alloy steel. The Ge addition to chromizing -siliconizing coating indeed increases the oxidation resistance of low alloy steel.

It is well known that the parabolic oxidation rate (K_P) obeys an Arrhenius-type equation :

$K_P = K_o \exp(-Q/RT)$

Where , K_0 is the pre-exponential factor, Q is the activation energy (J/mol), T is the temperature (K), and R is the universal gas constant (8.314 J/mol.K). The effective energy for Ge-doped chromizing-siliconizing can be calculated by plotting ln (K_P) vs. (1/T) in the temperature range (600-800^{o}C) as shown in Figure 7. For Ge-doped chromizing-siliconizing, K_p = 3x10^{-7} Exp (-10600/T) and the activation energy, Q (kJ/mol), is 88.2 (kJ/mol) **.** For chromizing -siliconizing [17], **Kp** = 9 x10^{-6} Exp (-12900/T) and the activation energy, Q (KJ/mol), is 107.200 (KJ/mol) .

The addition of Ge to the chromizing –siliconizing coating on low alloy steel will increase the oxidation resistance of low alloy steel. X-ray diffraction pattern for Ge-doped chromizing-siliconizing showed that the phase $CrSi_2$ was formed as in Figure 3. The peak of the phase of $CrSi_2$ was very sharp and high. The coating is considered to have good oxidation resistance performance because of the formation of $CrSi_2$ phase. Thus, during oxidation in air both phases SiO_2 and Cr_2O_3 will be formed. They will prevent the diffusion of the oxygen into the substrate. This coating was predominantly by the inward diffusion of Cr and Si. It was seen apparently in the cross-sectional image that the coatings were free from pack inclusions, which were known to be contained in the coatings that were formed by the outward growth mechanism. And in the X-ray diffraction pattern no peak about the pack inclusions was found.

Conclusions

The uncoated low alloy steel exhibits breakaway oxidation behavior when oxidized in air at 800 ^{o}C. The oxidation behaviors of the chromizing-siliconizing coated systems are parabolic at 800 ^{o}C. The Cyclic oxidation behaviors of the Ge- doped chromizing-siliconizing coated systems are parabolic in the temperature range 600-800 ^{o}C in air. The addition of Ge to the chromizing –siliconizing coating on low alloy steel will increase the oxidation resistance of low alloy steel because of the formation of both phases SiO_2 and Cr_2O_3. For Ge-doped chromizing-siliconizing, the activation energy, Q (kJ/mol), is 88.2 (kJ/mol)**.** For chromizing -siliconizing, the activation energy, Q (KJ/mol), is 107.200 (KJ/mol) .

References

1-.L.LShier, R.A. Jarman, G.T. Burstein, “Corrosion”, Vol.1, Metal /Environment Reactions, p.16-30, Butterworth-Heinemann Pub. Co. Oxford ,2000

2- D. H. Boone, *Mater. Sci. Technol* . Vol. 2, p. 220 ,1986.

3-R. Mevrel, C. Duret, and R. Pichoir, *Mater. Sci. Technol* . Vol.2 , p.201, 1986.

4- J. M. Molarius, A. S. Korhonen, E. Harju, and R. Lappalainen, *Surf. Coating Technol* . Vol.33, p.117, 1987.

5-G. W. Goward and D. H. Boone, *Oxid. Met.* Vol.3, p. 475, 1971.

6- E. Godlewska and K. Godlewski, *Oxid. Met.* Vol.22, p.117, 1984.

7- M.T. Kim, J.S. Jung, Surface and Coatings Technology, Vol.161, p. 218–223, 2002.

8- Rahmel and Tobolski , " Corrosion Behavior of Ferrite Steels on The Air Sides of Boiler Tubes in a Steam/Air Dual Environment", Materials at High Temperature, Vol.18,No.1, pp.51-56,2000.

9- Adachi and G.H. Meier, " Corrosion Behavior of Chromized and or Aluminized 2.25Cr-1Mo Steel in Medium-BTU Coal Gasifier Environments ", Surface and Coatings Technology, Vol.36, pp.49- 60,.1988,

10- Jyh-Wei Lee, Jenq-Gong Duh , Surface and Coatings Technology ,Vol. 177 –178, PP525–531, 2004.

11- G.W.Howard and L.W. Cannon, Trans. ASME Vol.110, p.150, 1988

12- M.A. Harper, R.A. Rapp, Oxid. Met. Vol. 42, p.303.1994.

13- X.R. Wan, W.M. Guo, Aviat. Prod. Eng._in Chinese. Vol.164 ,No.8, pp. 25-27, 1996.

14- X.R. Wan, Zh.Q. Bai, J. Chin. Soc. Corr. Prot._in Chinese. Vol. 17, PP. 494-497, 1997

15- P. Wei , X.R. Wan, "The effect of a coating heat-treatment on Cr-Si and Heat-treatment on the mechanical properties of Cr17Ni2 stainless steel, Surface and Coatings Technology Vol.132, pp.137-142, 2000.

16- H. Ho Park et al. ”Difusion Coatings for Iron Aluminide Halide-Activated Pack Cementation “, The Mineral, Metals & Materials Society, pp.347-359,1992,.

17- Abbas Khamas, "Effect of Chromizing –Siliconizing Process on Oxidation Properties of Low Alloy Steel", Ph.D. Thesis, University of Technology, Dept of Prod. Eng and Metallurgy, Baghdad Iraq, Sept 2007 .

18- N. Birks, and G.H. Meier, "Introduction to High Temperature Oxidation of Metals ", Edward Arnold Pub. Ltd. London. 1983.

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Table 1 Nominal composition of low alloy steel (Type T_{22}-ASTM)

Element	Fe	C	Mn	P_{max}	S_{max}	Si	Cr	Mo
Wt.%	Rem.	0.05-0.15	0.3-0.6	0.025	0.025	0.5max	1.9-2.6	0.87-1.13

Table 2 Spectrochemical analysis of low alloy steel (Type T_{22}-ASTM)

Element	Fe	C	Mn	P	S_m	Si	Cr	Mo	V	Ti
Wt.%	Rem.	0.06	0.35	0.012	0.011	0.46	1.96	0.91	0.002	0.01

Table(3) The Pack Mixture Composition and The Heating Cycle Used in Low Alloy Steel Type T_{22}-ASTM Pack Cementation

Pack Cementation Process	**Pack Cementation Wt.%**						**HoldingTemp.,Time**
	Cr	**Si**	**Ge**	**NaCl**	**NaF**	**SiO_2**	
Chromizing-Siliconizing	**16**	**6**	**-**	**2**	**2**	**74**	**1050°C for 6hr.**
Ge-doped chromizing -siliconizing	**16**	**6**	**1**	**2**	**2**	**73**	**1050°C for 6hr.**

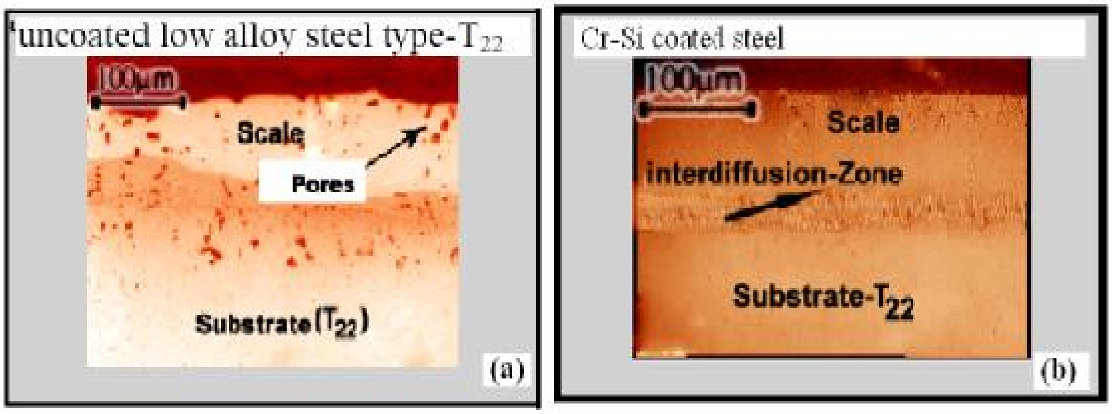

Figure 1 . LOM of low alloy steel type-T_{22} after cyclic oxidation in air at 800 °C for 100 hrs at 5 hrs cycle, (cross section views).(a) uncoated low alloy steel type-T_{22} , (b) chromizing- siliconizing low alloy steel

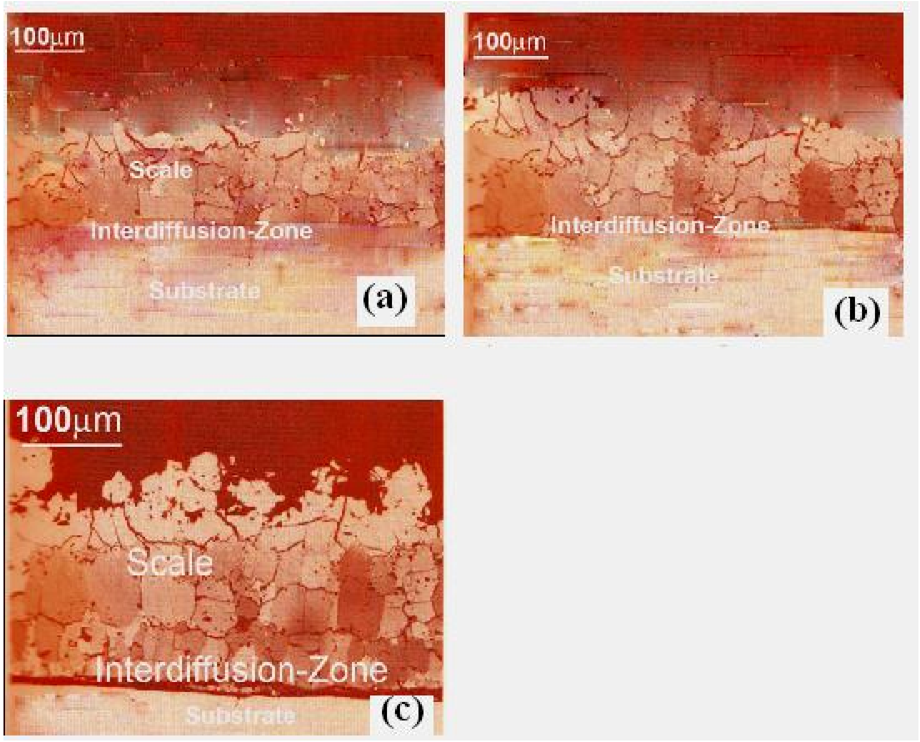

Figure 2. LOM of low alloy steel type-T_{22} coated with Ge- doped chromizing-siliconizing after cyclic oxidation in air for 100 hrs at 5 hrs cycle (cross section views). (a) 600 °C, (b) 700 °C, (c) 800 °C.

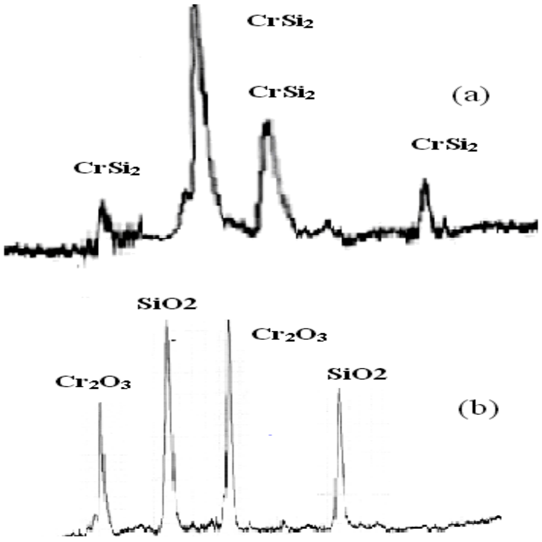

Figure 3. XRD-Phases of low alloy steel coated with Ge-doped Cr-Si .(a) after coating, (b) after oxidation in air at 800 °C.

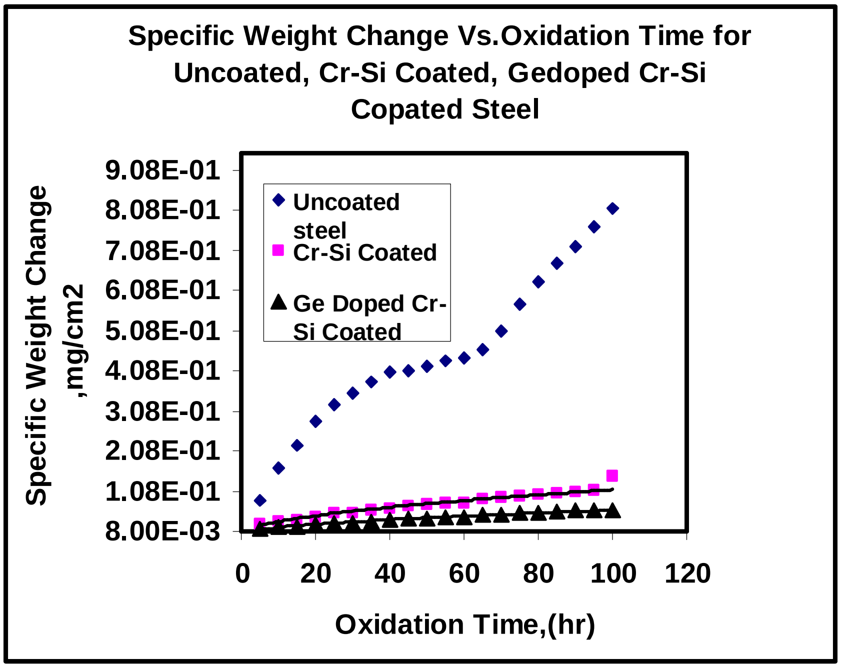

Figure 4. Specific weight gain vs. oxidation time at 800 °C during cyclic oxidation in air for 100hrs at 5hrs cycle for uncoated low alloy steel type-T_{22} , chromizing-siliconizing and Ge-doped chromizing-siliconizing

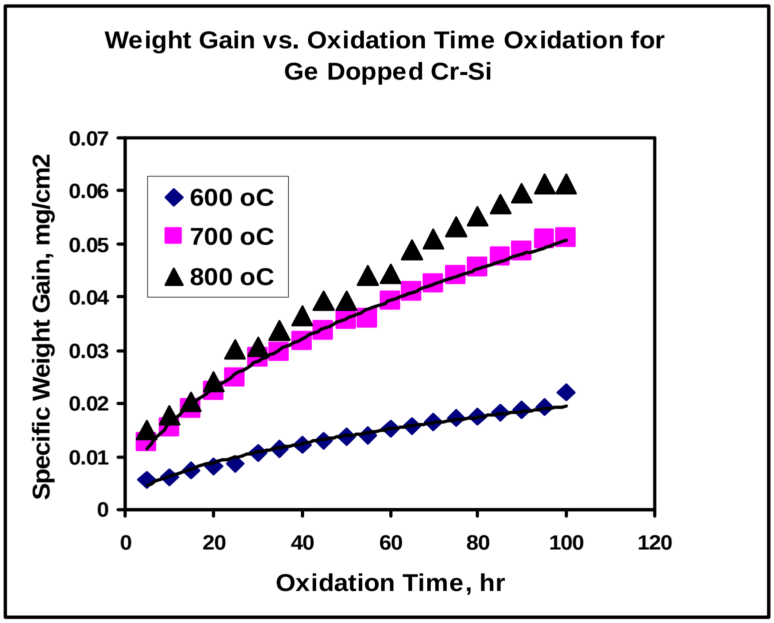

Figure 5. Specific weight gain vs. oxidation time at 600-800 °C during cyclic oxidation in air for 100hrs at 5hrs cycle for Ge-doped chromizing-siliconizing coated low alloy steel

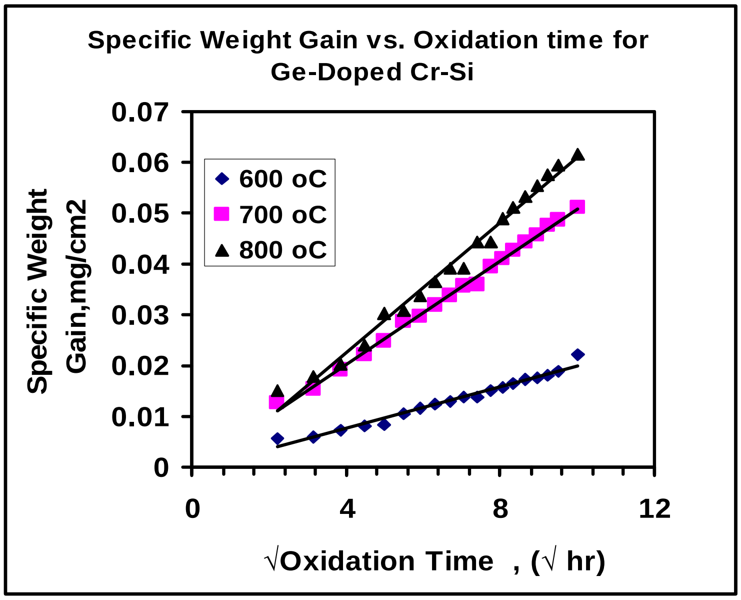

Figure 6. Specific weight gain vs. square root of oxidation time at 600-800 °C during cyclic oxidation in air for 100 hrs at 5hrs cycle for Ge-doped chromizing-siliconizing coated low alloy steel

Table 4. Parabolic rate constant K_P (gm^2/ cm^4 **sec**) for different coating systems

Coating	**Temp °C**	**K (mg/ cm^2 √hr)**	**n**	**Kp (gm^2/ cm^4 sec)**	**Reference**
Cr-Si coating	**800**	**0.0128**	**0.52**	**$4.55x10^{-10}$**	**Present work**
Ge-doped chromizing-siliconizing coating	**600**	**0.0021**	**0.49**	**$1.23x10^{-11}$**	**Present work**
	700	**0.0051**	**0.49**	**$7.23x10^{-11}$**	
	800	**0.0064**	**0.51**	**$1.14x10^{-10}$**	
Cr-Si coating	**600**	**0.0033**	**0.48**	**$3.03x10^{-11}$**	**Reference [17]**
	700	**0.0089**	**0.5**	**$2.20x10^{-10}$**	
	800	**0.0128**	**0.53**	**$4.0x10^{-10}$**	

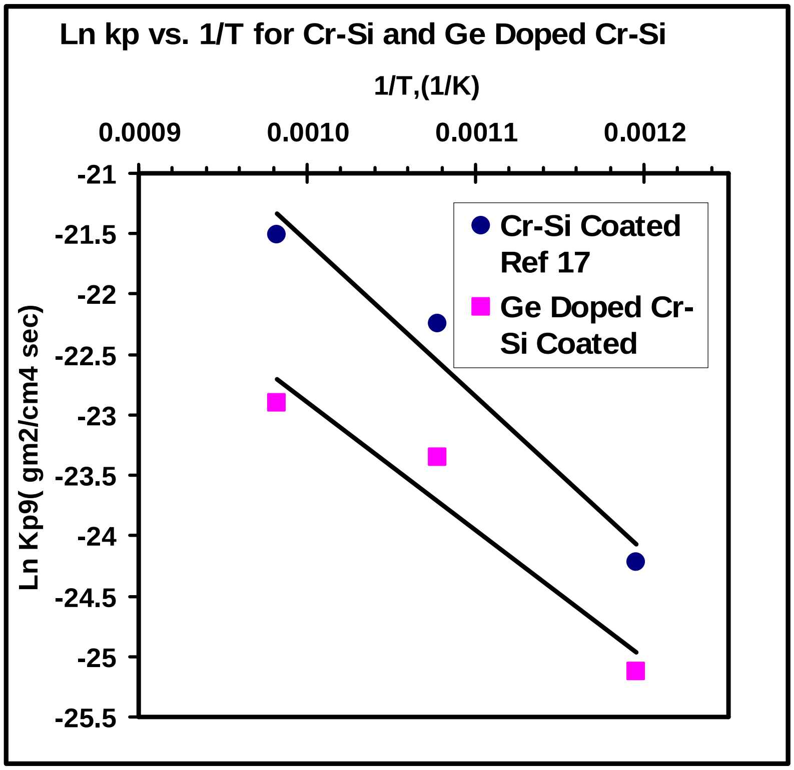

Figure 7 Parabolic rate constant vs. (1/T) for Ge-doped chromizing-siliconizing coated low alloy steel during cyclic oxidation in air for 100 hrs at 5hrs cycle , 600-800 °C.