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**Codeposition of chromium and silicon onto iron-base alloys via
pack cementation**

Harper, Mark Andrew, Ph.D.

The Ohio State University, 1992

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CODEPOSITION OF CHROMIUM AND SILICON ONTO
IRON-BASE ALLOYS VIA PACK CEMENTATION

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

by

Mark Andrew Harper, B.S., M.S.

* * * * *

The Ohio State University

1992

Dissertation Committee:

R.A. Rapp

Y. Sahai

K. Sandhage

Approved by

Advisor

Program in
Metallurgical Engineering

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VITA

May 24, 1959	Born - Augusta, Georgia.
June 1989	B.S. Metallurgical Engineering The Ohio State University Columbus, Ohio.
March 1991	M.S. Materials Science & Engineering The Ohio State University Columbus, Ohio.

PUBLICATIONS

- * P.A. Choquet, M.A. Harper, and R.A. Rapp, "Chromizing-Aluminizing and Chromizing-Siliconizing Coating of a Ferritic Steel", Proceedings of the 7th European Conference on Chemical Deposits from a Gas Phase, Perpignan, France, June 1989.
- * M.A. Harper and R.A. Rapp, "Codeposition of Chromium and Silicon in Diffusion Coatings for Iron-Base Alloys Using Pack Cementation", Fourth International Conference on Surface Modification Technologies, Paris, France, 1990.
- * M.A. Harper and R.A. Rapp, "Chromized/Siliconized Diffusion Coatings for Iron-Base Alloys by Pack Cementation", Paper Number 66, Corrosion 91, NACE, March 1991; Materials Performance, September (1991) 41-44.
- * M.A. Harper and R.A. Rapp, "Chromized/Siliconized Pack Cementation Diffusion Coatings for Heat Resistant Alloys", Proceedings of First International Conference on Heat Resistant Materials, ASM International, Fontana, WI, Sept. 1991.
- * R. Bianco, M.A. Harper, and R.A. Rapp, JOM, Vol. 43, No. 11 (1991) 20-25.

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ABSTRACT

The simultaneous deposition of Cr and Si into plain carbon, low-alloy, and austenitic steels using a halide-activated pack cementation process is described. Equilibrium partial pressures of gaseous species have been calculated using the ITSOL computer program to aid in designing specific processes required to codeposit the desired ratios of Cr and Si into a given alloy. The calculations indicate that NaCl-activated packs are chromizing while NaF-activated packs deposit more Si with less Cr. The use of a "dual activator" (e.g. NaF + NaCl) allows for the deposition of both Cr and Si in the desired amounts.

Single-phase ferritic coatings (150-250 microns thick) with a surface concentration of 20-35 wt% Cr and 2-4 wt% Si have been obtained in AISI 1018 steel, Fe-2.25Cr-1.0Mo-0.15C steel, and Fe-0.5Cr-0.5Mo-0.2C steel using packs containing a 90wt%Cr-10Si binary source alloy, a NaF+NaCl activator, and a silica filler.

Two-phase interdiffusion zones (approximately 75 microns thick) containing 20-25 wt% Cr and 2.0-2.4 wt% Si have been obtained in 304 stainless steel using packs containing a 90wt%Cr-10Si binary source alloy, a NaF activator, and an

alumina filler. The same pack chemistry allowed for the diffusion of Cr and Si into the austenitic solid solution of Incoloy 800 with no phase change occurring.

A coated Fe-2.25Cr-1.0Mo-0.15C sample with a surface concentration of Fe-34wt%Cr-3Si was cyclically oxidized in air at 700°C for over four months and 47 cycles. The weight gain was very low (<0.2 mg/cm²) with no scale spalling detected. Also, coated coupons of AISI 1018 steel and Fe-0.5Cr-0.5Mo-0.2C steel have shown excellent oxidation/sulfidation resistance in reducing, S-containing atmospheres at temperatures ranging from 400 to 700°C and in erosion and erosion-corrosion testing in air at 650 and 850°C.

Preliminary testing in aqueous solutions indicates coated coupons perform better than uncoated coupons but do not perform as well as 304 stainless steel.

CHAPTER I

INTRODUCTION

Pack cementation is a modified chemical vapor deposition process which consists of heating a closed/vented pack to an elevated temperature (e.g. 1323 K) for a given length of time (e.g. 16 hours) during which a diffusional coating is produced. The pack consists of four components: the substrate(s) or part(s) to be coated, the element(s) to be deposited (in the form of a powder masteralloy), a halide activator salt (e.g. NaF), and a powder filler (e.g. Al_2O_3 or SiO_2). An inert gas (e.g. argon) surrounds the pack. Upon heating at the elevated temperature, the activator salt reacts with the elements of the masteralloy to form metal halide vapors which diffuse to the substrate surface through the gas phase in the porous pack. At this surface, the reaction step resulting in the deposition of the desired element(s) may be somewhat complex, involving adsorption, dissociation, and/or surface diffusion of the molecular species¹.

An economical process to provide Fe-base alloys with corrosion-resistant coatings that can withstand high temperature environments such as air, combustion product gases, mixed O_2/S , O_2/C , and more complex multi-oxidant gases,

and corrosion by fused salts should find significant industrial application. Such a coating may also resist certain corrosive aqueous environments. Likewise, coating compositions which could provide superior oxidation and corrosion resistance with sufficient coating ductility might not exhibit adequate mechanical properties to satisfy the role of the base metal for a given application. This study demonstrates the use of a modified pack cementation method to produce adherent corrosion-resistant coatings on a variety of iron-base alloys.

To resist most corrosive environments, alloys involving an interactive use of two corrosion-resistant components generally are more effective than a simple binary alloy. Upon exposing an Fe-30wt%Cr-3Si alloy in a high-temperature oxidizing environment, a Cr_2O_3 scale forms initially, preventing both the rapid oxidation of Fe, and the internal oxidation of the Si. By its formation, the Cr_2O_3 scale reduces the oxygen activity at the scale-metal interface, thus allowing the thermodynamically more stable and very slow growing SiO_2 film to form beneath the Cr_2O_3 at steady state². However, excessively higher alloy contents of Cr and especially Si would lead to inadequate ductility and a propensity to form an embrittling sigma phase in service (see Figure 1). Currently, most commercial pack cementation coating processes involve the deposition of single elements (e.g. Al, Cr, or Si) and although coating processes involving

Figure 1. The Fe-Cr-Si ternary phase diagram at 900°C³.

two elements (e.g. Cr-Al or Al-Si) are advertised, usually complex two-step procedures are used to incorporate the elements sequentially into the substrate surface^{4,5}. Furthermore, the deposition of Cr during the coating of alloys containing carbon usually results in the formation of a chromium carbide layer (Cr_{23}C_6), which subsequently blocks the inward diffusion of Cr. However, the simultaneous introduction of Si during the coating process acts to push the carbon into the substrate because of a strong thermodynamic repulsion between Si and C and the transformation of the surface layer from austenite to ferrite. Because ferrite has a very low solubility for carbon, the outer carbide layer can be avoided.

A single-step process for codeposition of two elements in the desired concentration would reduce material, labor, time and energy, and would produce elemental distributions that would provide superior oxidation and corrosion resistance with adequate ductility⁶. Rapp, Wang, and Weisert⁷ developed procedures for the simultaneous codeposition of Cr and Al to produce Kanthal-like surface compositions (Fe-20wt% Cr-4.5Al) on iron and iron-base alloys. However, their processing procedure required a rotating, tumbling pack, which would prove impractical commercially. In the present work, the known beneficial effect of silicon in combination with

chromium in high temperature oxidation environments⁸ led to the development of a pack cementation coating process for various Fe-base alloys.

CHAPTER II

LITERATURE SURVEY

2.1 PACK CHROMIZING

The chromizing of steels was first reported in the literature in 1923⁹. The coatings were found to resist aqueous corrosion and were used to protect steam turbine blades. Currently, chromized coatings are used for hot corrosion resistance on gas turbine blades and vanes¹⁰, and for the water walls of utility boilers.

As shown in the Fe-Cr binary phase diagram¹¹ of Figure 2, for a coating temperature of 1050°C, a pure Fe substrate is austenite until a local Cr concentration at the surface reaches the boundary of the gamma loop (11.5 at%Cr). Enrichment to higher Cr concentrations results in the transformation of the surface layer from austenite to ferrite and a ferritic surface coating grows into the austenitic substrate. At the coating temperature, a ferrite-austenite epitaxial structural interface would exist along with a discontinuity in the Cr concentration profile because a concentration gradient is forbidden by the phase rule in a two-phase field in a binary system. Upon cooling, the ferrite-austenite interface retains the compositional

Figure 2. The Fe-Cr Binary Phase Diagram.

discontinuity when the austenitic substrate transforms to ferrite.

When chromizing carbon-containing steels, carbon from the substrate diffuses rapidly to the surface and reacts with Cr to produce Cr-carbides^{12,13} at the surface. Therefore, pack chromizing of steels requires a long time (approximately 18 hours) at a quite high temperature (1150°C) to permit the partial dissolution of chromium from the carbide and provide an adequate Cr solute profile beneath the carbide.

2.2 PACK SILICONIZING

There is little in the literature regarding the siliconizing of Fe-base alloys via pack cementation. Fitzer¹⁴ studied the siliconizing of pure Fe and steels using ferrosilicon masteralloys containing 6-20wt%Si, a NH_4Cl activator, a coating temperature of 1500°C, and diffusion times ranging from 5 to 30 hours. The study showed: 1) adherent, nonporous coatings containing 6-11wt%Si could be produced, 2) it was not possible to produce adherent, nonporous coatings with higher silicon contents, and 3) excessive outward growth occurred during the coating process. Thus siliconizing using pack cementation has not been adopted on any considerable scale in industry¹⁵.

2.3 OXIDATION OF Fe-Cr ALLOYS

Felton¹⁶ studied the oxidation of Fe-25wt%Cr and Fe-37.5wt%Cr at temperatures ranging from 650 to 900°C in a dry O₂ atmosphere (P_{O₂} = 0.13 atm). The oxide formed on both of these alloys was identified as Cr₂O₃. Francis and Whitlow¹⁷ oxidized an Fe-25wt%Cr alloy at 1000°C in 1 atm of reactor grade CO₂ (50 ppm O₂, 10 ppm H₂O); a Cr₂O₃ scale formed on this alloy. An Fe-30wt%Cr alloy was oxidized in O₂ (P_{O₂} = 0.13 atm) at 1000°C by Tedmon¹⁸. The scale formed during the oxidation consisted of Cr₂O₃ with less than 1 wt%Fe₂O₃. A (Cr,Fe)₂O₃ scale with less than 2 wt%Fe was detected on alloys (Fe-14wt%Cr and Fe-27.4wt%Cr) oxidized by Wood and Whittle¹⁹ in 1 atm O₂ at 800 and 1000°C. Graham et al.²⁰ oxidized Fe-25wt%Cr in O₂ (100 ppm O₂, balance Ar) at 1100°C. Secondary ion mass spectrometry sputter profiles indicated a Cr₂O₃ scale with less than 1%Fe present in the outer part of the oxide layer. The alloy composition, temperature, gas atmosphere, and gravimetric rate constants are listed in Table 1. An Arrhenius plot of the rate constants is shown in Figure 3. The dotted lines in the figure show the range of scatter on the reported rate constant values.

2.4 OXIDATION OF Fe-Cr-Si ALLOYS

Wood et al.²¹ oxidized Fe-29.2wt%Cr-5.1Si, Fe-26.4wt%Cr-0.97Si, and Fe-14.0wt%Cr-3.7Si alloys in 1 atm of oxygen at 1000 and 1200°C. All of the alloys formed continuous SiO₂

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Figure 3. Arrhenius plot for the reported gravimetric rate constants for the growth of Cr_2O_3 on binary Fe-Cr alloys.

layers at the Cr_2O_3 -alloy interface, identified using electron probe microanalysis.

Miner and Nagarajan^{22,23} studied the oxidation/sulfidation of Fe-18wt%Cr alloys containing 0.5 to 2.0wt%Si at 982°C. All of the alloys were oxidized in air, in an $\text{H}_2/\text{H}_2\text{O}$ environment ($\text{Po}_2=10^{-18}$ atm) and corroded in an $\text{H}_2/\text{H}_2\text{O}/\text{H}_2\text{S}$ environment ($\text{Po}_2=10^{-18}$ atm, $\text{P}_{\text{S}_2}=10^{-6}$ atm) after preoxidizing in air. The alloys formed a non-continuous subscale of silica when oxidized in air or the low Po_2 environment; however, during exposure of the alloys to the sulfur-containing environment Fe-sulfides were found to form under the Cr_2O_3 scale and the silica subscale.

Stott et al.²⁴ oxidized Fe-14wt%Cr-3Si, Fe-14wt%Cr-10Si, and Fe-28wt%Cr-1Si in 1 atm of oxygen at 1000°C. The addition of 1wt% Si into the Fe-28wt%Cr alloy caused a marked reduction of the oxidation rate (see Figure 4²⁵) particularly by facilitating the development of the Cr_2O_3 scale and by the formation of SiO_2 precipitates which eventually formed a healing layer by inward and lateral growth at the alloy/scale interface. Similar behavior was observed for the Fe-14wt%Cr-3Si alloy but the healing layer formed at much shorter times for the Fe-14wt%Cr-10Si alloy. Scale spallation was extensive for this high Si alloy during cooling from 1000°C to room temperature.

Robertson and Manning²⁶ found that additions of Si improved greatly the oxidation resistance of low Cr steels in

a 2% CO-CO₂ mixture (reduced k_p by a factor of up to 10^4) at 575-650°C and protected the alloys from breakaway corrosion. The minimum Si content for this effect varied from 0.3wt% Cr for an Fe-11wt%Cr alloy, to 2.5-3.0wt%Si for pure Fe itself.

Newcomb and Stobbs²⁷ conducted a transmission electron microscopy (TEM) study on an Fe-11wt%Cr-1.1Si alloy oxidized in a 2% CO-CO₂ atmosphere at 600°C for 3088 hours. A thin continuous (30 nm thick) silica film was found using the TEM.

The addition of Si to Fe-Cr binary alloys shows the potential for a coating containing Cr and Si. Furthermore, a coating would provide excellent high temperature oxidation resistance while eliminating the detrimental effects of alloying with Si, i.e. reduction in alloy ductility and the propensity of forming a brittle sigma phase.

Figure 4. Weight gain versus time for an Fe-28wt%Cr binary alloy and an Fe-26wt%Cr-1Si alloy oxidized in 1 atm of O_2 at 1000°C^{23} .

CHAPTER III

THERMODYNAMIC ANALYSIS OF THE PACK

For the halide-activated pack cementation process, the refractory enclosure containing the substrate(s), the masteralloy, the activator salt(s), and the filler, can be treated as a closed system in thermodynamic equilibrium. The activator reacts with the elements in the source alloy to form the metal halide vapors, which then diffuse through the porous pack to the substrate where the metallic elements are codeposited if the two vapor species have comparable arrival fluxes resulting from comparable vapor pressures. If the vapor pressures are not within one to two orders of magnitude, then the deposition of one element will dominate (e.g. either chromizing or else siliconizing).

For codeposition of chromium (Cr) and silicon (Si) onto an Fe-base alloy, disproportionation reactions, displacement reactions, and alkali vapor reactions might occur as indicated in Figure 5.

The upper limit for the composition(s) for the coating element(s) at the substrate surface is set by the thermodynamic limitation that the activity of the element(s) cannot be greater than its activity in the masteralloy⁶. To

A. Disproportionation Reactions

B. Displacement Reactions

C. Alkali Vapor Reactions

Figure 5. Possible deposition reactions in a pack containing a Cr-Si masteralloy and a NaCl activator.

calculate the equilibrium partial pressures of the halide species, the activities of the coating elements must be known. Therefore, a knowledge of the activities for the coating elements in the source masteralloy is essential to design the codeposition of elements into the substrate.

Figure 6 shows the equilibrium phase diagram for the Cr-Si binary system²⁸. The two-phase regions marked 'A', 'B', 'C', and 'D' are introduced for later reference.

Eremenko et al.²⁹ have studied the Cr-Si system and measured the Gibbs energies of formation for the Cr silicides as a function of temperature from 973 to 1123 K (Table 2). The present study involves a temperature of 1323 K; however, from 1123 to 1323 K, no phase transformation exists, so that the equations for the Gibbs energies were assumed to hold for these higher temperatures.

From calculations of the Gibbs energies, the activities of Cr and Si in the two-phase regions were determined. An example calculation of the activities is shown in Appendix A. Table 3 lists the activities of Cr and Si for the two-phase regions, and Figure 7 shows a plot of $-\log(\text{activity})$ versus the mole fraction of Si at 1323 K. The activities for Cr and Si are constant in the two-phase fields.

In the present study, the calculation of the partial pressures was performed using the computer program STEPSOL³⁰. This program calculates the equilibrium partial pressures for a given temperature and is based on the minimization of the

Figure 6. Equilibrium phase diagram for the Cr-Si system.

Table 2. Gibbs energies of formation of the Cr silicides from 973 to 1123 K (T is in degrees kelvin).

Cr_3Si :	$-138.57 + 0.014(T)$	(2.34) kJ/mol
Cr_5Si_3 :	$-273.8 + 0.006(T)$	(3.68) kJ/mol
CrSi :	$-58.75 - 0.003(T)$	(0.67) kJ/mol
CrSi_2	$-79.92 - 0.0026(T)$	(0.84) kJ/mol

Table 3. Activities calculated for Cr and Si for the two-phase regions of Cr-Si binary system at 1323 K.

<u>Two Phase Region</u>	$\underline{a}_{\text{Cr}}$	$\underline{a}_{\text{Si}}$
<u>Cr</u> + Cr_3Si	0.54	1.3×10^{-4}
Cr_3Si + Cr_5Si_3	0.12	1.1×10^{-2}
Cr_5Si_3 + CrSi	0.03	0.11
CrSi + CrSi_2	0.02	0.15
CrSi_2 + <u>Si</u>	5.1×10^{-4}	1.00

Figure 7. Plot of $-\log(\text{activity})$ versus mole fraction of Si at 1323 K.

Gibbs energy of the system and the conservation of mass for each element³¹.

Four Cr-Si compositions: 90wt% Cr-10wt% Si, 80Cr-20Si, 70Cr-30Si, and 60Cr-40Si, and four activators: NaCl, NaF, FeCl₂, and CrCl₂ were investigated by calculation.

Calculations were performed for pack compositions consisting of:

- 1) 75.0 wt% filler (Al₂O₃ or SiO₂)
- 2) 23.0 wt% masteralloy
- 3) 2.0 wt% halide activator salt (NaCl, NaF, FeCl₂, or CrCl₂)

From these calculations, appropriate combinations for the activator salt, the composition of the masteralloy, and the choice of filler were determined. The details and assumptions for these calculations have been published by Kung and Rapp³².

Figures 8 through 11 show the variation of the partial pressures of the metal halides as a function of the silicon activity, for equilibrium in the pack. The four sets of data points marked on the figures correspond to the two-phase regions marked in Figure 6. For Figs. 8-11, the SiO₂ filler has been assumed to react to form Na₂Si₂O₅(l).

Figure 8 shows the equilibrium condition for a pack with a NaCl activator and silica filler at 1323 K. The data points for masteralloy 'A' indicate that the CrCl₂ vapor species dominate the silicon chloride species. Therefore, a pack

Figure 8. Equilibrium partial pressures of metallic halides in NaCl activated packs containing Cr-Si masteralloys at 1323 K and SiO₂ filler.

Figure 9. Equilibrium partial pressures of metallic halides in NaF activated packs containing Cr-Si masteralloys at 1323 K and SiO₂ filler.

Figure 10. Equilibrium partial pressures of metallic halides in FeCl_2 activated packs containing Cr-Si masteralloys at 1323 K and SiO_2 filler.

Figure 11. Equilibrium partial pressures of metallic halides in CrCl₂ activated packs containing Cr-Si masteralloys at 1323 K and SiO₂ filler.

containing a 90wt% Cr-10 Si masteralloy and a NaCl activator at 1323 K should be a chromizing pack, i.e. deposit Cr and little (less than 1wt%) or no Si. However, a pack containing masteralloy 'B', 'C', or 'D' should codeposit Cr and Si in comparable concentrations.

The equilibrium partial pressures for packs containing a NaF activator and silica filler are shown in Figure 9. The Si fluoride partial pressures dominate in this pack, thus predicting the deposition of more Si and little or no Cr.

Figure 10 shows the partial pressures for an FeCl_2 -activated pack at 1323 K. Comparable partial pressures exist for CrCl_2 and SiCl_3 at the region corresponding to the two-phase field of Cr_3Si and Cr_5Si_3 . Similar results are found in Figure 11 which shows the partial pressures for a CrCl_2 -activated pack at 1323 K.

Figure 12 shows the partial pressures of CrCl_2 and CrCl_3 of Figure 8 (NaCl activated pack) superimposed on the SiF_2 and SiF_3 partial pressures of Figure 9 (NaF activated pack). This figure is inserted to show the possibility of using a "dual activator" for the chromizing/siliconizing process. That is, the chloride would carry the Cr to the substrate surface and the fluoride would do the same for the Si. To fine-tune such a codeposition pack, the relative amounts (activities) of NaCl and NaF might be varied. Figure 13 shows such a plot where the partial pressures were calculated as a function of the mole fraction of NaF for a pack containing a 90wt%Cr-10Si

Figure 12. A simple superposition of CrCl_2 and CrCl_3 partial pressures from NaCl-activated pack (Figure 8) on the SiF_2 and SiF_3 partial pressures from a NaF activated pack (Figure 9).

Figure 13. Equilibrium partial pressures of metallic halides as a function of the mole fraction of NaF present in a NaF+NaCl activated pack with a 90wt%Cr-10Si masteralloy and SiO_2 filler at 1323 K.

masteralloy and SiO_2 filler diffused at 1323 K. Although the SiCl_4 and SiF_4 have a relatively high partial pressure, these two vapor species are assumed not to play a role in the deposition process. This is due to their inability to deposit Si through a displacement or disproportionation reaction. The same is true for CrCl_4 . To our knowledge, a mixture (or solution) of two halide activators is not used today by commercial cementation pack coating vendors.

Figures 14 and 15 show the partial pressures of NaCl- and NaF-activated packs respectively, with alumina entered as the filler. As shown in Figs. 14 and 15, in comparison to Figs. 8 and 9, the partial pressures of both the Si and Cr halides are lowered by approximately two orders of magnitude upon the substitution of Al_2O_3 for SiO_2 as the filler. These increases in partial pressures for both the Si and Cr halides for the SiO_2 filler result from the stability (and presumed formation) of $\text{Na}_2\text{Si}_2\text{O}_5(l)$ at the process temperature. If $\text{Na}_2\text{Si}_2\text{O}_5(l)$ is not entered into the calculation for the pack containing the silica, the calculated partial pressures for the Si and Cr halides are virtually the same as for the alumina filler calculation. However, the consideration of $\text{Na}_2\text{Si}_2\text{O}_5(l)$ formation in the calculation for the silica filler produces the values shown in Figures 8 and 9. The explanation for this behavior is as follows. Sodium is consumed in the formation of $\text{Na}_2\text{Si}_2\text{O}_5(l)$. The only source of Na in the pack is $\text{NaCl}(l)$

Figure 14. Equilibrium partial pressures of metallic halides in NaCl activated packs containing Cr-Si masteralloys at 1323 K and Al₂O₃ filler.

Figure 15. Equilibrium partial pressures of metallic halides in NaF activated packs containing Cr-Si masteralloys at 1323 K and Al_2O_3 filler.

or NaF(l) , and the reaction of silica to form $\text{Na}_2\text{Si}_2\text{O}_5\text{(l)}$ displaces Na from the activator, while the chlorine or fluorine is released into the gas phase. In this way, an increase in the chlorine/fluorine activity in the pack occurs. Therefore, the vapor pressures of the Si- and Cr-halide species are increased significantly. Incidentally, SiO_2 is not used commercially, to our knowledge, as a "reactive" filler in cementation packs.

Thus computer-assisted thermodynamic calculations provide guidance in choosing an appropriate masteralloy, activator, and filler combination for the codeposition of Cr and Si into a given alloy. In this work, the codeposition of Cr and Si into plain carbon and low alloy steels, in the desired proportions, was accomplished by using a 90wt%Cr-10Si masteralloy, a "dual activator" of NaF+NaCl , and the "reactive" silica filler. This method is both unique and novel in that the exact role of the chloride carrying the Cr and the fluoride carrying the Si has never been explained in the literature, the use of the two activators in the same pack has never been successfully applied before (to our knowledge), and the importance of the filler has never been realized or published.

CHAPTER IV

EXPERIMENTAL PROCEDURE AND MATERIALS

4.1 PACK PREPARATION

The cementation pack contains four components: 1) a powder filler, 2) a masteralloy, 3) an activator, and 4) the substrate or part to be coated. A silica powder (80-200 mesh) obtained from Davison Chemical or an alumina powder (80-200 mesh) obtained from Fischer Sci. Co. was used as the fillers in various experimental packs. The masteralloys were obtained from Consolidated Astronautics and consisted of four compositions: 90 Cr-10wt%Si, 80 Cr-20wt%Si, 70 Cr-30wt%Si, 60 Cr-40wt%Si. Anhydrous, reagent-grade NaCl (Fischer), NaF (Fischer), FeCl_2 (Morton Thiokol), and CrCl_2 (Morton Thiokol) were used as the activator salts.

The pack, consisting of 75wt% filler, 23wt% masteralloy and 2wt% activator, was thoroughly mixed by tumbling the powders in a plastic bottle on rollers for 8 to 12 hours.

Seven different substrate materials were used; their nominal compositions are listed in Table 4:

- Interstitial-free steel (IF steel)
- T22 steel
- T2 steel

- AISI 1018 steel
- 304 stainless steel
- 316 stainless steel
- Incoloy 800

Armco Steel (R. E. Hook) provided the interstitial-free steel. The T22 steel was supplied by B.F. Goodrich and the T2 steel by Babcock & Wilcox (S. Kung). The AISI 1018 steel was purchased from a local supplier (Art Iron Steel & Aluminum Service). Shell Development Corp. (R. John) provided the 304, 316, and Incoloy 800 samples. Alloy coupons were cut using a water-cooled abrasive wheel saw and polished on SiC paper to 240 grit. Initial weights and dimensions were recorded.

The mixed pack was poured into an alumina crucible, 3.1 cm I.D. x 6.4 cm. Several substrate coupons were buried in the pack and the crucible was closed and sealed with an alumina lid using an alumina-based cement. The seal was sufficiently porous to permit some loss of gas upon heating and some exchange with the Ar surrounding the crucible. Thus Ar acted as a diffusion medium, but no powder was lost when the crucible was placed on its side for the coating process.

Table 4. Nominal substrate compositions (wt%).

Alloy	Cr	Ni	Mn	Si	Mo	C	Fe	Other
IF	.02	--	.19	---	---	.01	bal	.07 Ti .08 Nb .06 Al
T22	2.25	--	.45	0.5	1.0	0.15	bal	
T2	0.5	--	.65	0.25	0.5	0.21	bal	
1018	--	--	0.8	<0.6	---	0.18	bal	<0.6 Cu
304	19	10	1.5	0.5	---	.05	bal	---
316	17	12	1.5	0.5	2.5	.05	bal	---
Incoloy 800	21	33	.75	---	---	.05	bal	0.38 Al 0.38 Cu

4.2 EXPERIMENTAL COATING APPARATUS

The sealed crucible was placed inside an alumina tube (4.6 cm I.D.) and positioned in the uniform heating zone of a horizontal resistance-heated tube furnace. A gas-tight seal was maintained by sealing the ends of the alumina tube and using Cajon ultra-torr adapters and flexible tubing to permit the entry of a thermocouple and gas flow through the seals.

The crucible temperature was monitored using a chromel-alumel (Type K) thermocouple in contact with the crucible and connected to the furnace temperature controller.

Prepurified argon flowed through the alumina tube after passing through a desiccant and oxygen getter. The exit flow of the Ar was bubbled through a heavy oil at atmospheric pressure and exhausted through a chemical hood. A schematic of the furnace setup is shown in Figure 16.

A 2- to 3-hour heat-up time was required to raise the temperature from room temperature to the desired process temperature (1050 to 1150°C). The process temperature was maintained for times ranging from 6 to 24 hours. Once the desired coating time was obtained, the crucible was allowed to furnace cool for approximately 4 hours (300°C). The crucible was taken out of the furnace, the lid removed, and the coated substrates removed from the pack and cleaned with a wire brush. The weight of the coated samples after the coating process was recorded.

4.3 EXPERIMENTAL OXIDATION APPARATUS

Coated alloys were cyclically oxidized by placing the samples in the uniform heating zone of a horizontal resistance-heated furnace with both ends of the furnace open to air. Periodically, the samples were removed from the furnace, cooled to room temperature, and weighed using a Mettler AJ100 balance.

Isothermal oxidation of coated samples was performed using a CAHN TG171 thermogravimetric apparatus. The sample was placed on the hangdown wire of the TG171 and the furnace was raised to a position which placed the sample in the uniform heating zone. The furnace was heated to 700°C while air was passed through the furnace tube. The change in weight as a function of time during the experiment was stored on the hard drive of the computer used to control the TG171. The data from the experiment (weight, time, and temperature) were taken and analyzed/plotted using a data analysis and graphical plotting program. A schematic diagram of the TG171 is shown in Figure 17.

4.4 COATING AND OXIDE SCALE CHARACTERIZATION

The coated samples were cross-sectioned using a low speed diamond saw and prepared for optical and scanning electron microscopy using standard metallographic techniques. The

1. Ar cylinder
2. dehumidifier
3. deoxidizer
4. heating tape
5. thermocouple
6. seal assembly

7. alumina reaction tube
8. furnace
9. alumina crucible
containing pack
10. oil reservoir

Figure 16. Schematic diagram of furnace setup.

1. Microbalance	8. Furnace switch
2. Stand	9. Status lights
3. Cooling fan	10. Elevator controls
4. Cooling fan switch	11. Thermocouple connector
5. Furnace	12. Leveling feet
6. Temperature display	13. Thermocouple connector (TG-171)
7. Gas ports	16. Vacuum port
	17. Weight display

Figure 17. Schematic diagram of the thermogravimetric analysis apparatus used for isothermal oxidation.

alloys 304SS, 316SS, and Incoloy 800 were etched using a modified acetic-glyceregia (4 ml HCl, 2 ml HNO₃, 2 ml acetic acid, 2 ml glycerol). The coated plain carbon and low alloy steel alloys were etched using nital (90 ml methyl alcohol, 10 ml HNO₃).

A Nikon Epiphot-TME inverted microscope was used for the optical microscopy, and micrographs were taken with Polaroid Type 55 film. Concentration profiles of the coating cross-sections were determined with energy dispersive spectroscopy (EDAX-SW9100) on a JEOL-JXA-35. The composition at a given point was determined by comparing the counts for the various elements detected with the EDS detector with counts stored in a file for a high silicon steel (Fe-2.89wt%Si) standard and an AISI 446 stainless steel (Fe-24.2wt%Cr) standard. Both standards were obtained from the National Institute of Standards and Technology. The use of these standards decreased the Si concentration error from approximately 20% to less than 5% and the Cr concentration error from 10% to less than 5% as determined by examining alloys with a known Cr and Si content.

Scanning electron microscopy of oxidized samples was performed with a JEOL-840F scanning electron field emission microscope. A Scintag PAD V theta - 2-theta x-ray diffractometer was used for x-ray diffraction of the samples before and after coating, and after oxidation. A surface analysis of coated and oxidized samples was conducted with a

Physical Electronics Industries 660 Scanning Auger Microprobe
at the High Temperature Materials Laboratory at the Oak Ridge
National Laboratory.

CHAPTER V

RESULTS AND DISCUSSION

5.1 COATING RESULTS

5.1.1 LOW ALLOY AND PLAIN CARBON STEELS

After performing the STEPSOL calculations and studying the plots of partial pressures versus activity of Si (Figures 8 through 11), it was concluded that a pack consisting of an FeCl_2 or CrCl_2 activator and an 80wt%Cr-20Si masteralloy at 1323 K would achieve codeposition of chromium and silicon. Therefore experiments were started with these components. However, the initial batch of 80wt%Cr-20Si masteralloy powder ordered and received had an actual composition of 85wt%Cr-15Si, which was not learned until the next batch of masteralloy was ordered and received. Thus numerous experiments were performed using an 85wt%Cr-15Si masteralloy.

Plate I shows the process parameters, morphology, and composition for an interstitial-free (IF) steel specimen coated using the 85wt%Cr-15Si masteralloy, FeCl_2 activator, and Al_2O_3 filler diffused at 1323 K for 16 hours. The substrate surface experienced severe attack and resembled one which had undergone degradation by chlorine environments^{33,34}. This "swiss cheese" morphology is

Plate I. Microstructure and concentrations of coated IF steel using 85wt%Cr-15Si masteralloy and FeCl_3 activator diffused at 1323 K for 16 hours (Al_2O_3 filler).

Point # →	1	2
Cr (wt%)	31.0	11.3
Si (wt%)	1.0	0.9

Weight Gain = -43.7 mg/cm^2

believed to result from the high FeCl_2 vapor pressure at the surface, with the substrate losing iron by reactive vaporization with the chloride vapors. The loss of iron results in the weight-loss for the coupon noted in Plate I. Although the Cr concentration was suitably high (31wt%), the outer perforated layer plus the desire for a higher silicon content (2-4 wt%) required an adjustment in the process parameters to obtain a more suitable coating.

To reduce the FeCl_2 vapor pressure, a slightly more stable halide salt (CrCl_2) was used as an activator. Plate II shows the result of coating an IF specimen at 1030°C. The coating still exhibited some surface roughness, and the silicon concentration was low. A run at 1000°C using the same pack composition was performed to reduce the halide vapor pressures. The corresponding results are shown in Plate III. The surface was smooth and no voids were present. However, the relatively thin coating and the low silicon content made this coating inadequate. Furthermore, because of the low silicon in the coatings produced from the FeCl_2 - and CrCl_2 -activated packs, these two activators used individually could not produce suitable coatings since a silicon concentration of more than 1.0 wt% was desired.

In an effort to overcome the problem of low silicon concentrations, two activators in the same pack were used to increase the silicon content to 2.0-4.0wt%. Because NaF is a siliconizing activator, and a chloride activator tends to be

Plate II. Microstructure and concentrations of coated IF steel using 85wt%Cr-15Si masteralloy and CrCl_2 activator diffused at 1303 K for 24 hours (SiO_2 filler).

Point # →	1	2	3	4	5
Cr (wt%)	40.6	31.0	22.9	17.2	0.6
Si (wt%)	1.0	0.9	0.8	0.7	0.7

Weight Gain = -8.0 mg/cm^2

Plate III. Microstructure and concentrations of coated IF steel using 85wt%Cr-15Si masteralloy and CrCl_2 activator diffused at 1273 K for 24 hours (SiO_2 filler).

Point # →	1	2	3	4	5
Cr (wt%)	36.7	31.9	19.1	15.3	0.4
Si (wt%)	0.0	0.5	0.6	0.6	0.5

Weight Gain = N/A

chromizing, as determined from Figure 12, the possibility of chromizing/siliconizing in a single pack containing both NaF and a given chloride activator (e.g. NaCl) was discovered. In other words, the NaF could be used to deposit silicon and NaCl to deposit chromium. Plate IV shows the process parameters, microstructures and compositions for an IF specimen coated using a "dual activator" consisting of a mechanical mixture of 50mol%NaF+50%NaCl. As shown by the concentrations, the silicon content was increased to 3.0-4.0wt% at the outer surface and the chromium content was still high.

At this time in the research a new batch of masteralloy was received and the discrepancy in composition for the first batch of masteralloy was realized. Thus the previous results had in fact been obtained with a single-phase masteralloy having a composition that fell in a one-phase field (between 'A' and 'B' shown in Figure 3). Because of the large change in Cr and Si activities across a given intermetallic compound, coupled with the difficulty of producing a masteralloy with such an exact composition, attempts were made to develop a coating process that used a masteralloy composition within a two-phase field, either region 'A' or 'B'.

Plate V shows the microstructure and compositions of a T22 alloy coated with an 80wt%Cr-20Si masteralloy, SiO₂ filler, and a NaCl activator. As shown in the plate, the chromium content is less than desired. Thus this masteralloy

Plate IV. Microstructure and concentrations of coated IF steel using 85wt%Cr-15Si masteralloy and NaF+NaCl activators (50wt%NaF-50NaCl mechanical mixture) diffused at 1303 K for 24 hours (SiO_2 filler).

Point # →	1	2	3	4	5
Cr (wt%)	39.6	30.4	16.8	10.1	0.5
Si (wt%)	3.9	3.3	2.7	2.3	0.6

Weight Gain = N/A

Plate V. Microstructure and concentrations of coated T22 steel using 80wt%Cr-20Si masteralloy and NaCl activator diffused at 1323 K for 16 hours (SiO_2 filler).

100 μm

Point # →	1	2
Cr (wt%)	10.9	10.0
Si (wt%)	4.9	4.2

Weight Gain = -12.6 mg/cm^2

was not suitable since a low chromium content was obtained with the use of a chromizing NaCl activator.

Plate VI shows the microstructure and compositions of a T22 alloy coated with a 90wt%Cr-10Si masteralloy, SiO₂ filler, and a NaCl activator. With this masteralloy, the use of a chromizing activator resulted in a high concentration of chromium in the coating. Plate VII shows a 1018 steel coated with the same pack composition except that the NaF activator was used. As shown in Plate VII, the desired Si content was achieved but the Cr composition was lower than desired.

At this time the partial pressures shown in Figure 12, coupled with the results of Plate VI and VII, led to the use of a "dual activator" to obtain the desired concentrations of chromium and silicon. The result of a run using a molten 90mol%NaF-10NaCl activator is shown in Plate VIII. The coating contains approximately 3wt% Si at the surface but the Cr content was still higher than desired. A Cr content of 35wt% or more introduces the formation of sigma phase. The chromium content was lowered by using an activator with less NaCl. Plate IX shows the microstructure and compositions for a coated T22 alloy using a 95mol%NaF-5NaCl molten activator. As shown in this plate, the Cr content was lowered from 46wt% using a 90mol%NaF-10NaCl activator (Plate VIII) to 38wt% using a 95mol%NaF-5NaCl. A further reduction in the Cr content was achieved on a T2 alloy using a 97mol%NaF-3NaCl activator.

Plate VI. Microstructure and concentrations of coated T22 steel using 90wt%Cr-10Si masteralloy and NaCl activator diffused at 1323 K for 16 hours (SiO_2 filler).

100 μm

Point # →	1	2	3	4
Cr (wt%)	49.0	29.5	10.7	2.6
Si (wt%)	1.9	1.6	1.4	1.1

Weight Gain = +17.9 mg/cm^2

Plate VII. Microstructure and concentrations of coated 1018 steel using 90wt%Cr-10Si masteralloy and NaF activator diffused at 1323 K for 16 hours (SiO_2 filler).

100 μm

Point # →	1	2	3	4	5
Cr (wt%)	8.8	8.8	8.5	7.4	6.2
Si (wt%)	2.6	2.8	2.7	2.5	2.1

Weight Gain = +9.6 mg/cm^2

Plate VIII. Microstructure and concentrations of coated T22 steel using 90wt%Cr-10Si masteralloy and 90mol%NaF-10NaCl activator diffused at 1323 K for 16 hours (SiO_2 filler).

Point # →	1	2	3
Cr (wt%)	45.9	25.7	15.5
Si (wt%)	3.1	2.4	1.9

Weight Gain = +18.4 mg/cm²

Plate IX. Microstructure and concentrations of coated T22 steel using 90wt%Cr-10Si masteralloy and 95mol%NaF-5NaCl activator diffused at 1323 K for 16 hours (SiO_2 filler).

Point # →	1	2	3	4	5	6
Cr (wt%)	37.8	23.8	16.5	14.8	9.0	2.4
Si (wt%)	3.7	3.0	2.5	2.5	2.1	1.3

Weight Gain = +28.1 mg/cm²

Plates X and XI show the results of a coated T2 alloy and AISI 1018 steel, respectively, using this activator.

As shown in the plates, large grain growth perpendicular to the substrate surface occurs during the coating process. This evidently results from the diffusion of Cr and Si along a preferred direction in the body-centered cubic lattice of the ferrite coating. This preferred direction extends inward beyond the compositional interface, resulting in an epitaxial relationship between the grains in the coating and the uncoated substrate. Also, the fine ferrite grains at the immediate surface in Plate VII are the result of some outward coating growth contribution that occurs, as has been confirmed by marker observations.

X-ray diffraction showed the presence of the Fe-Cr sigma phase (see Figure 18) for coatings containing excess Cr, e.g. the coating shown in Plate VIII. Coatings with less than 30wt%Cr were body-centered cubic, i.e. ferrite, as shown in Figure 19. Also, the coatings with 30wt%Cr-3Si at the surface were relatively ductile, exhibiting a Vickers hardness of approximately 240 (+10) kgf/mm² measured at 30 microns beneath the surface. The uncoated substrate near the center of the coupon had a Vickers hardness of approximately 105 kgf/mm². Microhardness measurements were conducted on chromium carbide (Cr₂₃C₆) for comparison. These values exceeded 1000 kgf/mm².

Plate X. Microstructure and concentrations of coated T2 steel using 90wt%Cr-10Si masteralloy and 97mol%NaF-3NaCl activator diffused at 1323 K for 16 hours (SiO_2 filler).

Point # →	1	2	3	4
Cr (wt%)	27.7	21.2	15.5	9.0
Si (wt%)	3.3	2.8	2.5	1.8

Weight Gain = +21.6 mg/cm²

Plate XI. Microstructure and concentrations of coated 1018 steel using 90wt%Cr-10Si masteralloy and 97mol%NaF-3NaCl activator diffused at 1323 K for 16 hours (SiO_2 filler).

100 μm

Point # →	1	2	3	4	5
Cr (wt%)	26.8	26.2	20.6	15.8	8.4
Si (wt%)	2.6	2.5	2.4	2.0	1.4

Weight Gain = +24.5 mg/cm^2

Figure 18. Intensity versus 2-theta for x-ray diffraction scan of coated T22 steel coupon similar to Plate VIII.

Figure 19. Intensity versus 2-theta for x-ray diffraction scan of coated T2 steel coupon similar to Plate X.

Thus through the calculation of equilibrium partial pressures, as shown in Figures 8 through 11, and analyzing the trends shown in these figures (i.e. realizing the importance of using a silica filler and the use of a fluoride plus chloride activator), a method to codeposit Cr and Si in the desired proportions was developed. The ability to achieve surface compositions of approximately Fe-25 to 35wt%Cr-2 to 4Si on low alloy and plain carbon steels was demonstrated. Again, this procedure is unique by its: 1) ability to deposit Cr and Si in the desired proportions in a single isothermal step, one pack process, and 2) the elimination of the outer brittle chromium carbide layer that usually forms on carbon-containing alloys when Cr is introduced at the surface. In addition, because of the inward diffusion of the Cr and Si, little or no pack entrapment occurred during the coating process. This eliminates the concern of coating degradation resulting from masteralloy or filler particles embedded within the coating.

5.1.2 AUSTENITIC ALLOYS

Plates XII and XIII show an initial attempt to chromize/siliconize 304 stainless steel and Incoloy 800 using a 90wt%Cr-10Si masteralloy, NaF activator, and SiO₂ filler. Because these alloys already contain sufficient Cr, only a Si addition may be adequate for oxidation resistance. This run produced surface compositions containing excess chromium and

thus a brittle coating as determined using microhardness testing. Although NaF is a siliconizing activator, the masteralloy powder becomes depleted of Si during the coating process, leaving essentially pure Cr particles. Thus an increase in Cr is observed due to its high activity near the substrate surface.

The importance of the filler used in the coating process is realized by comparing Figures 8 and 15. To test this variable specifically, an Al_2O_3 filler was used to lower the partial pressures of the Cr halides in the pack, thereby reducing the flux of Cr to the substrate and preventing excess Cr in the coating. Plates XIV and XV show the microstructures and compositions of 304 SS and Incoloy 800 coupons coated with such packs. As seen in Plate XIV, the 304 SS has a coating thickness of approximately 75 microns and consists of a two-phase microstructure. For Incoloy 800, both chromium and silicon were diffused into the austenitic solid solution (Plate XV) without a phase change.

The two phases of the 304 SS coating were identified as alpha-ferrite plus retained austenite using x-ray diffraction (see Fig. 20). Also, microhardness measurements showed a Vickers hardness of approximately 375 kgf/mm^2 for the ferritic regions and 250 kgf/mm^2 for the adjacent austenitic regions. The substrate near the center of the sample had a hardness of

Plate XII. Microstructure and compositions of coated 304 SS using 90wt%Cr-10Si masteralloy and NaF activator diffused at 1050°C for 16 hours (SiO_2 filler).

Point #⇒	1	2	3	4	5	6
Cr (wt%)	39.9	34.3	33.0	29.7	29.4	19.0
Si (wt%)	3.7	3.1	3.2	3.0	3.1	1.0
Ni (wt%)	6.9	7.7	8.1	8.3	8.3	9.7

Weight Gain = +14.3 mg/cm²

Plate XIII. Microstructure and compositions of coated Incoloy 800 using 90wt%Cr-10Si masteralloy and NaF activator diffused at 1050°C for 16 hours (SiO_2 filler).

100 μm

Point #→	1	2	3	4
Cr (wt%)	58.5	49.8	27.7	22.3
Si (wt%)	6.2	4.5	2.8	1.8
Ni (wt%)	14.6	16.3	30.8	30.7

Weight Gain = +7.6 mg/cm^2

Plate XIV. Microstructure and concentrations for various locations of coated 304 SS using 90Cr-10Si masteralloy and NaF activator diffused at 1150°C for 16 hours (Al_2O_3 Filler).

100 μm

Point # →	1	2	3	4	5
phase →	ferrite	austenite	ferrite	austenite	aust
Cr (wt%)	25.4	20.1	26.2	20.3	20.4
Si (wt%)	2.2	2.0	2.4	2.1	2.1
Ni (wt%)	7.8	11.7	7.4	11.7	11.2

Weight Gain = +5.5 mg/cm^2

Plate XV. Microstructure and compositions of coated Incoloy 800 using 90wt%Cr-10Si masteralloy and NaF activator diffused at 1150°C for 16 hours (Al_2O_3 filler).

100 μm

Point #→	1	2	3	4	5	6	7
Cr (wt%)	26.0	27.0	25.3	25.1	23.1	21.4	20.9
Si (wt%)	5.0	3.9	3.8	3.8	3.2	2.3	1.8
Ni (wt%)	28.3	27.9	28.9	28.1	29.6	30.3	31.2

Weight Gain = +4.9 mg/cm²

Figure 20. Intensity versus 2-theta for x-ray diffraction scan of coated 304 SS coupon similar to Plate XIV.

150 kgf/mm². Adequate ductility should be expected from this coating. A Vickers hardness of 180 kgf/mm² was measured near the surface of the coated Incoloy 800.

5.2 HIGH TEMPERATURE CORROSION RESULTS

5.2.1 CYCLIC OXIDATION RESULTS

A coated T22 steel coupon with a microstructure and coating composition similar to Plate IX was cyclically oxidized in air at 700°C for over four months (47 cycles). Each cycle consisted of removing the sample from the furnace, allowing it to air cool to room temperature, weighing the sample on a Mettler AJ100 balance, and placing the sample back into the furnace. As shown in Figure 21, the coupon exhibited extremely slow oxidation kinetics with no detectable scale spalling. The much more rapid isothermal oxidation kinetics for an uncoated T22 steel³⁵ or for a Cr₂O₃-forming Fe-25wt%Cr binary alloy³⁶ are included in Fig. 21 for comparison. This comparison between the coated T22 and the Fe-25wt%Cr-3Si alloy shows the extremely beneficial effect of the Si addition in the coating. The exact role of the Si will be discussed in Section 5.3.

Figure 21. Plot of weight-gain versus time for the cyclic oxidation in air at 700°C of a coated T22 steel with a surface composition of 34Cr-3Si. Each indicated point represents the weight-gain measured after cooling from 700°C to room temperature.

Coated coupons of 304 stainless steel and Incoloy 800 as described in Plates XIV and XV were cyclically oxidized in air at 1035°C. Figure 22 shows the weight-gain versus time for these two coated alloys, and for two uncoated alloys as a comparison. The coated 304 SS coupon exhibited a low weight-gain and very little scale spalling (within the sensitivity of measurement for the Mettler AJ100 balance). The coated Incoloy 800 showed an improvement over the uncoated sample, but the amount of spalling was still significant (about 1% of the surface area of the sample).

5.2.2 ISOTHERMAL OXIDATION RESULTS

Isothermal oxidation in air at 700°C of a coated AISI 1018 steel coupon with a surface concentration of Fe-20wt%Cr-3Si was performed using a CAHN TG171 microbalance. Figure 23 shows a plot of weight-gain versus the square-root of time. The parabolic rate constant was $4.6 \times 10^{-15} \text{ gm}^2/\text{cm}^4\text{s}$ as determined from the slope of the curve shown in Figure 23. The weight-gain shown during the ramp up to 700°C was observed during a "blank" run on the TG171, i.e. a run with no specimen, and was taken as an artifact of the equipment.

Figure 22. Plot of weight-gain versus time for the cyclic oxidation in air at 1035°C of coated and uncoated 304 SS and Incoloy 800. Each indicated point represents the weight-gain measured after cooling from 1035°C to room temperature.

Figure 23. Plot of weight-gain versus the square root of time for the isothermal oxidation in air at 700°C of a coated 1018 steel with a surface composition of 32Cr-3Si.

Figure 24 shows a comparison of this rate constant to values published in the literature for the growth of Cr_2O_3 . Deal and Groves³⁷ give a value of $9.4 \times 10^{-15} \text{ gm}^2/\text{cm}^4\text{s}$ for the growth of SiO_2 on pure Si. Thus the parabolic rate constant for oxide growth on the coated samples is approximately one order of magnitude slower than that for the growth of chromia and of the same magnitude as the rate constant for the growth of silica on Si.

5.2.3 EXTERNAL CORROSION TEST RESULTS

To test the chromized/siliconized coatings in environments that more closely simulate industrial applications coupons of T22, T2, and AISI 1018 were coated and supplied to various companies and laboratories for high temperature corrosion testing.

Coated T22 coupons were sent to Shell Development in Houston, TX and tested isothermally at temperatures ranging from 400 to 700°C in a reducing sulfur-containing gas (medium BTU fuel). The coatings performed better than typical heat-resistant austenitic alloys. In the uncoated state, such low-alloy steels would suffer catastrophic sulfidation.

Coupons of coated T22 were sent to the Foster Wheeler Corporation in Livingston, NJ and tested in a severe synthetic

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fly ash environment. The very severe test consisted of coating the samples with an ash made of 5wt% K_2SO_4 , 5wt% Na_2SO_4 , 30wt% Al_2O_3 , 30wt% SiO_2 , and 30wt% Fe_2O_3 and passing a gas of 15.6% CO_2 , 10.0% H_2O , 3.6% O_2 , 1.0% SO_2 , and a balance of N_2 over the samples. The test ran for 600 hours, and two test temperatures were investigated, 650 and 700°C. Visual examination showed the coated coupons performed comparable to Alloy 690 (Ni-29wt%Cr-9Fe) alloy at the 650°C, but at 700°C the samples were severely corroded and did not perform well. However, out of twenty-three alloys tested at 700°C only two did perform well: Alloy 690 and Alloy 671 (Ni-50wt%Cr).

Chromized/siliconized samples of AISI 1018 steel were sent to Babcock & Wilcox in Alliance, OH for testing in a reducing, sulfur-containing gas at isothermal temperatures ranging from 500 to 700°C. The coatings were reported to perform comparable to or better than chromized alloys. Also, T2 samples supplied by Babcock & Wilcox were chromized/siliconized and tested in a coal-fired low NO_x environment produced in a burner-rig facility. The reducing environment, produced by burning coal containing 3.5% sulfur (Illinois Peabody #6 coal), simulated the combustion of cyclone boilers. The sample temperature was maintained at 427p28 °C. A plot of the metal wastage from the wall thickness of the samples as a function of exposure time is shown in Figure 25³⁸. The leading edge curve shown in the figure represents the side of the coupon that directly faced

the flue-gas flow direction and the trailing edge was 180° away from the leading edge. The chromized/siliconized T2 samples performed much better than uncoated plain carbon steel, T22 steel, or even 304 SS. Both of the Babcock & Wilcox tests exposed the coated coupons to a nominally reducing gas thus showing the coatings are sulfidation resistant.

Samples of AISI 1018 steel were coated, sent to the Institute of Paper Science and Technology at Georgia Tech in Atlanta, GA and tested in a Kraft process-type gaseous environment of 1% H₂S, 1% O₂, 2% H₂O, 10% CO₂, with balance N₂. The test temperature was 440°C. After exposure for 72 hours, the weight loss of a coated 1018 sample was 0.44 mg/cm². Uncoated AISI 1018 steel samples in the same environment had a weight loss of 22.3 mg/cm² after 72 hours. Also, uncoated 304 stainless steel had a weight loss of 1.1 mg/cm² after 72 hours exposure.

Chromized/siliconized coupons of AISI 1018 steel and T22 steel were sent to the Lawrence Berkeley Laboratory in Berkeley, CA for erosion and erosion-corrosion testing. The specimens were eroded by angular SiO₂ particles of average size 150 microns, at a particle velocity of 20 m/s, and at impact angles of 30° and 90°. The erosion time was 5 hours. Erosion wastages were measured by weight loss and cross-sectional thickness losses. The samples were tested at 25, 650, and 850°C. Figure 26 shows the thickness loss for the

various tested materials. The chromized/siliconized samples performed substantially better than uncoated 304 SS, chromized/aluminized 304 SS, uncoated 410 SS, chromized/aluminized 410 SS, chromized 1018 steel, and chromized T22 steel. Thus the chromized/siliconized samples performed better than all other coatings tested. The results of the outside testing are summarized in Table 5.

5.2.4 TECHNOLOGY TRANSFER

The technical transfer of this coating procedure to Babcock & Wilcox has been completed. A tube panel consisting of three T2 tubes was chromized/siliconized at the Alliance Research Center and installed into the lower furnace of East Bend 2, a Cincinnati Gas and Electric boiler. The tubes were 2.45 m long with a 7.5 cm O.D. An initial trial run using a 90wt%Cr-10Si masteralloy, a 98wt%NaF-2%NaCl activator, and a silica filler produced coatings exhibiting low Cr (<10wt% Cr) and chromium carbide precipitates in the coating (see Plate XVI). To increase the Cr and eliminate the carbide precipitates, an activator containing more NaCl (95wt%NaF-5%NaCl) was used and pure Si powder (1 wt% of pack) was added to the pack mixture to ensure that Si was deposited at the substrate early in the coating run. Because carbon and silicon exhibit a thermodynamic repulsion between each other, this Si addition acted to "push" the carbon inward and reduce the carbide precipitates. Plate XVII shows the coating

Table 5. Qualitative results from companies.

COMPANY/ COATED ALLOY	ATMOSPHERE	RESULTS
Shell Development T22	isothermal (400-700°C) reducing, S-containing gas (medium BTU fuel)	coatings performed better than typical heat-resistant austenitic alloys
Foster Wheeler T22	synthetic ash (containing 5wt% K ₂ SO ₄ , 5wt% Na ₂ SO ₄ , 30wt% Al ₂ O ₃ , 30wt% SiO ₂ , and 30wt% Fe ₂ O ₃) plus 15.6% CO ₂ , 10.0% H ₂ O, 3.6% O ₂ , 1.0% SO ₂ , balance N ₂ at 650°C and 700°C	- at 650°C (below melting temperature of sulfate in ash) coatings performed comparable to Incoloy 690 (Ni-29Cr-9Fe) - at 700°C (above melting temperature of sulfate in ash) coatings did not perform well
Babcock & Wilcox T2	isothermal (500-700°C) reducing, S-containing gas	chromized/siliconized coatings are performing comparable to or better than chromized coatings
Institute of Paper Science and Technology 1018	1% H ₂ S, 1% O ₂ , 2% H ₂ O, 10% CO ₂ , balance N ₂ gas at 440°C for 72 hours, Kraft process gas	-coated 1018 lost 0.44 mg/cm ² -uncoated 1018 lost 22.3 mg/cm ² -uncoated 304 SS lost 1.1 mg/cm ²
Lawrence Berkeley Laboratory T22 and 1018	erosion and erosion-corrosion by angular 150 micron SiO ₂ particles at 650°C and 850°C	the erosion and erosion-corrosion resistance of chromized/siliconized coupons was much better than those of uncoated alloys, chromized, and chromized/aluminized alloys

Plate XVI. Microstructure of T2 tube coated by Babcock & Wilcox using a 90wt%Cr-10Si masteralloy, 98wt%NaF-2%NaCl activator, and a silica filler diffused at 1150°C for 4 hours (Surface concentration: Fe-7.4wt%Cr-2.7Si).

100 μm

Plate XVII. Microstructure and compositions of T2 tube coated by Babcock & Wilcox using a 90wt%Cr-10Si masteralloy, 95wt%NaF-5%NaCl activator, pure Si powder (1wt% of pack), and a silica filler diffused at 1150°C for 7 hours (Surface concentration: Fe-16.6wt%Cr-3.6Si).

Point # →	1	2	3	4	5	6
Fe (wt%)	79.8	80.7	83.4	86.0	87.9	97.1
Cr (wt%)	16.6	16.4	14.2	11.9	10.0	2.2
Si (wt%)	3.6	2.9	2.4	2.1	2.1	0.7

produced, after these adjustments were made, on the panel installed in the East Bend 2 boiler. The surface concentration was improved to approximately Fe-16.6wt%Cr-3.6Si and should perform well in the fireside corrosion environment. Sections of this panel will be removed every 18 months for corrosion evaluation.

In summary, Cr/Si coated coupons of T22, T2, and 1018 steel have shown excellent isothermal and cyclic high temperature oxidation resistance and generally perform better than other coatings and expensive alloys. A patent prepared by Babcock & Wilcox but submitted by The Ohio State University to the U.S. Patent Office is pending.

5.3 AQUEOUS CORROSION RESULTS

During the downtime of boilers, petrochemical reactors, etc., condensation may lead to the aqueous corrosion of materials which were designed for high temperature oxidation. For example, an alumina-forming alloy may exhibit very slow scale growth kinetics at high temperatures (500-1000°C) in an oxidizing/sulfidizing atmosphere, and yet suffer from poor aqueous corrosion resistance at room temperature due to chloride attack of the Al component. Although aqueous corrosion resistance may be of secondary importance, materials used in these systems should exhibit protective behavior.

Preliminary testing was conducted on coated plain carbon steel coupons. An uncoated AISI 1018 steel sample, a coated

1018 sample with a surface concentration of Fe-9wt%Cr-3Si, and a coated 1018 sample with a surface concentration of Fe-30wt%Cr-3Si were tested in a 3.5% NaCl aqueous solution open to air at room temperature. Scanning polarization experiments were performed on each sample. Plots of the linear polarization results are shown in Figures 27 through 29. Note the change in the abscissa scale for Figure 29. The Tafel polarization curves are shown in Figures 30 through 32. The data for these experiments are tabulated in Appendix B.

The linear polarization data were obtained by applying an overvoltage of 10 mV (in steps of 2 mV) more noble and more active than the corrosion potential and manually reading the applied current from the microammeter. As shown in Fig. 29, some vertical sets of data points resulted from the reduced corrosion of the Fe-30wt%Cr-3Si sample. The Tafel polarization curves were obtained by applying 200 mV of overvoltage (in steps of 10 mV) more noble and more active than the corrosion potential and recording the corresponding applied current.

The corrosion current for a given sample at the corrosion potential can be obtained using the equation³⁹:

$$\frac{\Delta E}{\Delta i_{app}} = \frac{\beta_a \beta_c}{2.3 (i_{corr}) (\beta_a + \beta_c)} \quad (5.1)$$

where $\Delta E/\Delta i_{app}$ is the slope of the linear polarization curve, β_a and β_c are the Tafel slopes for the anodic and cathodic reactions, respectively, and i_{corr} is the corrosion current.

Figure 27. Linear polarization curve of uncoated 1018 steel tested in a 3.5% NaCl aqueous solution at room temperature.

Figure 28. Linear polarization curve of coated 1018 steel (surface concentration Fe-9wt%Cr-3Si) tested in a 3.5% NaCl aqueous solution at room temperature.

Figure 29. Linear polarization curve of coated 1018 steel (surface concentration Fe-30wt%Cr-3Si) tested in a 3.5% NaCl aqueous solution at room temperature.

Figure 30. Tafel polarization curve for uncoated 1018 steel sample tested in 3.5% NaCl aqueous solution at room temperature ($E_{corr} = -673$ mV).

Figure 31. Tafel polarization curve for coated 1018 steel (surface concentration Fe-9wt%Cr-3Si) sample tested in 3.5% NaCl aqueous solution at room temperature ($E_{corr} = -610 \text{ mV}$).

Figure 32. Tafel polarization curve for coated 1018 steel (surface concentration Fe-30wt%Cr-3Si) sample tested in 3.5% NaCl aqueous solution at room temperature ($E_{corr} = -458 \text{ mV}$).

The slopes of the linear polarization curves, and the Tafel slopes are shown in the figures. The corresponding corrosion rates in mils per year (mpy) can be determined from the following expression based on Faraday's law³⁷:

$$\text{Corrosion penetration rate} = K a i / n D \quad (5.2)$$

where a is the atomic weight of the metal; i is the current density in $\mu\text{A}/\text{cm}^2$; n is the number of electrons lost (charge valence); D is the density in g/cm^3 ; and K is a constant. The atomic weight, valence charge, and density of pure Fe were used for the corrosion rate calculations shown in Table 6. The constant K equals 0.129 when calculating mpy. The Fe-30Cr-3Si sample exhibits very low corrosion in this environment, almost two orders of magnitude lower than the uncoated or poorly coated steel.

A coated 1018 steel sample with a surface concentration of Fe-20wt%Cr-3Si was tested in an 1 N H_2SO_4 aqueous solution at room temperature. Anodic polarization curves for exposure times of 4 hours, 6 hours, 12 hours, and 48 hours are shown in Figs. 33 through 36, respectively. As a comparison, Figure 37⁴⁰ shows an anodic polarization curve for 304 SS in 1 N H_2SO_4 . The coated 1018 steel coupon exhibited a higher critical current density and a higher minimum passive current density for steady-state corrosion in a passive state.

Table 6. List of corrosion rates for samples tested in 3.5% NaCl aqueous solution at room temperature.

Sample	$\Delta E/\Delta i_{app}$ (mV/uA cm ⁻²)	β_a (mV/dec.)	β_c (mV/dec.)	i_{corr} (uA/cm ²)	corr. rate (mpy)
1018	1.74	77.1	840	17.6	8.1
Fe-9Cr-3Si	2.49	83.6	2235	14.1	6.5
Fe-30Cr-3Si	55.0	29.9	321	0.216	0.1

Figure 33. Anodic polarization curve of coated 1018 sample (surface concentration Fe-20wt%Cr-3Si) after 4 hours exposure in 1 N H₂SO₄ at room temperature.

Figure 34. Anodic polarization curve of coated 1018 sample (surface concentration Fe-20wt%Cr-3Si) after 6 hours exposure in 1 N H₂SO₄ at room temperature.

Figure 35. Anodic polarization curve of coated 1018 sample (surface concentration Fe-20wt%Cr-3Si) after 12 hours exposure in 1 N H₂SO₄ at room temperature.

Figure 36. Anodic polarization curve of coated 1018 sample (surface concentration Fe-20wt%Cr-3Si) after 48 hours exposure in 1 N H₂SO₄ at room temperature.

A visiting researcher at OSU (Xiaoru Wan) has chromized/siliconized an Fe-1.05wt%Cr-1.1Si-1.6Ni-0.95Mn-0.3C high strength steel producing a surface concentration of 34wt%Cr-3.9Si. Samples of this coated steel have been placed in a 0.5 M H_2SO_4 aqueous solution at room temperature for weight loss analysis. After 2 months of exposure this coupon has shown no evidence of attack while an uncoated sample was totally dissolved in 1 day.

In conclusion, the chromized/siliconized samples showed excellent corrosion resistance in the 3.5% NaCl solution. However, in a 1N H_2SO_4 aqueous solution the 30Cr/3Si coatings were less resistant than 304 SS. Higher levels of Cr and Si seem needed in H_2SO_4 . These preliminary results show Cr/Si coatings exhibit improved aqueous corrosion resistance over uncoated plain carbon steels and show no harmful effects in general corrosion resulting from the Si addition.

5.3 OXIDATION MECHANISM STUDY

Figure 38 shows a plot of intensity versus 2-theta for an x-ray diffraction (XRD) scan of a coated 1018 steel coupon oxidized at 700°C for 164 hours. As shown in the diagram, the major peaks for alpha-iron and Cr_2O_3 are present. Figure 39 shows an XRD scan for a similar coupon oxidized at 700°C for 1100 hours. The peaks for alpha-iron and Cr_2O_3 , plus peaks showing the presence of FeCr_2O_4 , are seen for this extended time at high temperature. These samples were oxidized for the

Figure 38. Plot of intensity versus 2-theta for the x-ray diffraction of a coated 1018 steel coupon with a surface concentration of 32Cr-3Si oxidized in air at 700°C for 164 hours.

Figure 39. Plot of intensity versus 2-theta for the x-ray diffraction of a coated 1018 steel coupon with a surface concentration of 32Cr-3Si oxidized in air at 700°C for 1100 hours.

purpose to identify the oxide so that no weight-gain data or total weight changes were recorded.

Preliminary evidence for a slower growing silicon oxide beneath the outer chromia was deduced from results of the cyclic oxidation test described, as follows. Once steady-state oxidation occurs for a coated coupon the rate of weight-gain is extremely slow (see Figure 21 after 100 hours). If this slow oxidation resulted from the growth of an outer chromia scale, then removal of this scale and return of the coupon into the furnace at 700°C would result in a repeat of rapid transient oxidation of the sample until steady state oxidation occurred again. However, upon removing the outer scale using an ultrasonic cleaner (95% of the external surface appeared free of any oxide scale) and placing the sample back into the furnace for 24 hours, no transient oxidation occurred. In other words, the rate of weight-gain after the removal of the chromia scale was the same as before the removal of the chromia scale, so the oxidation is not limited by the growth of the chromia film at the surface.

Plate XVIII shows a spalled region of a coated 1018 steel coupon after isothermal oxidation at 700°C for 1100 hours and cooling to room temperature, whereby spalling occurred. Plate XIX shows a higher magnification of the spalled region in Plate XVIII. A "maximum thickness" for the growth of a silica film at 700°C for 1100 hours was calculated to be approximately 0.5 microns. Three regions are labeled in this

Plate XVIII. Secondary electron image of spalled region of coated 1018 steel coupon isothermally oxidized for 1100 hours.

Plate XIX. Higher magnification of spalled region in Plate XVIII showing regions 'a', 'b', and 'c'.

micrograph. The region labeled 'a' has a smooth non-faceted appearance, region 'b' has a faceted appearance, and the region marked 'c' is characteristic of a grain boundary. These three regions, plus the outer oxide scale, were examined using Auger electron spectroscopy in the High Temperature Materials Laboratory at Oak Ridge National Laboratory. Iron, chromium, and silicon were the elements present at regions 'a' and 'b', but silicon was not identified in the form of SiO_2 . Thus the slow oxidation kinetics shown by these coated coupons cannot be definitely ascribed to the growth of a thin silica film at the Cr_2O_3 /alloy interface. Auger analysis of region 'c' showed the presence of carbon, implying chromium carbides were present at the grain boundaries.

At this time the exact role of Si in the reduction of the oxidation kinetics has not been demonstrated. At temperatures below 800°C , Fe-Cr-Al alloys are not generally used since the formation of Al_2O_3 does not occur at these low temperatures. However, the oxidation/sulfidation results of the coated coupons in this study, and the results published by Robertson and Manning²⁶ on the oxidation of Fe-Cr-Si alloys, suggest the formation of SiO_2 does occur at lower temperatures. Given that the activation energy for the formation of SiO_2 is less than that for Al_2O_3 , the presence of SiO_2 at lower temperatures is more feasible. However, a thin silica film has not been identified and further study is needed to characterize the oxidation mechanism for these coatings.

CHAPTER VI
SUMMARY AND CONCLUSIONS

1. Computer-assisted thermodynamic calculations of various halide-activated cementation packs indicate that:
 - * Packs containing a chloride activator and a chromium-rich masteralloy will deposit Cr and little or no Si, i.e a chromizing pack.
 - * Packs containing a fluoride activator and a chromium-rich masteralloy will deposit less Cr and more Si.
 - * Packs containing some ratio of a fluoride+chloride activator, i.e. a "dual activator", will deposit the desired amount of Cr and Si.
 - * A silica filler reacts with the Na from the NaF and NaCl to form $\text{Na}_2\text{Si}_2\text{O}_5$ and raise the fluoride and chloride activity in the pack. The increase in fluoride and chloride activity results in an increase of the Cr and Si halides partial pressures in the pack.
2. Coatings were achieved on several Fe-base alloys using the pack cementation process. The results are summarized below.
 - * AISI 1018 steel, Fe-2.25Cr-1.0Mo-0.15C (T22) steel, and Fe-0.5Cr-0.5Mo-0.2C (T2) steel were successfully

chromized/siliconized with approximately 27wt%Cr-3Si at the surface. The coatings were produced using a 90wt%Cr-10Si masteralloy, 97mol%NaF-3NaCl activator, and silica filler diffused at 1323 K for 16 hours.

- * Incoloy 800 and 304 SS were successfully chromized/siliconized (surface concentration: Fe-28wt%Ni-26Cr-5.0Si) using a 90wt%Cr-10Si masteralloy, NaF activator, and alumina filler diffused at 1423 K for 16 hours. The Cr and Si were diffused into the austenitic solid solution of the Incoloy 800 with no phase change occurring. A two-phase (ferrite plus retained austenite) coating was produced on the 304 SS.

3. Coated coupons were tested in various oxidizing and oxidizing/sulfidizing high temperature environments. The results are summarized below.

- * A coated Fe-2.25Cr-1.0Mo-0.15C steel with a surface concentration of Fe-34wt%Cr-3Si exhibited extremely slow oxidation kinetics during cyclic oxidation in air at 700°C. After 47 cycles and 4 1/2 months exposure at 700°C the coupon gained less than 0.2 mg/cm².
- * The gravimetric rate constant of 4.6×10^{-15} gm²/cm⁴s was measured for a coated 1018 steel sample isothermally oxidized in air at 700°C. This value is approximately one order of magnitude lower than values published in the literature for the growth of Cr₂O₃ on chromia forming alloys.

- * Coated coupons of 304 SS and Incoloy 800 performed better than uncoated coupons in cyclic oxidation in air at 1035°C.
- * Coated Fe-2.25Cr-1.0Mo-0.15C coupons tested in a reducing, S-containing gas at 400 to 700°C performed better than typical heat-resistant alloys.
- * Coated Fe-2.25Cr-1.0Mo-0.15C coupons tested in a synthetic ash (5wt% K_2SO_4 , 5wt% Na_2SO_4 , 30wt% Al_2O_3 , 30wt% SiO_2 , and 30 wt% Fe_2O_3) and 15.6% CO_2 , 10.0% H_2O , 3.6% O_2 , 1.0% SO_2 , balance N_2 gas atmosphere at 650°C performed comparable to Incoloy 690 (Ni-29wt%Cr-9Fe). In the same ash and gaseous atmosphere at 700°C the coatings did not perform well.
- * Coated AISI 1018 steel samples tested in 1% H_2S , 1% H_2O , 10% CO_2 , balance N_2 gas at 440°C for 72 hours (Kraft process gas) lost 0.44 mg/cm². Uncoated coupons of 1018 lost 22.3 mg/cm² and 304 SS samples lost 1.1 mg/cm².
- * Coated AISI 1018 and Fe-2.25Cr-1.0Mo-0.15C steel coupons tested in erosion and erosion-corrosion testing (angular 150 micron SiO_2 particles at room temperature, 650°C, and 850°C) performed superior to other chromized alloys, chromized/aluminized alloys, and uncoated alloys.
- * Coated AISI 1018 steel samples tested in a 3.5% NaCl aerated aqueous solution at room temperature exhibited

superior corrosion resistance to uncoated 1018. The corrosion current for the coated sample was 0.216 $\mu\text{A}/\text{cm}^2$ versus 17.6 $\mu\text{A}/\text{cm}^2$ for an uncoated 1018 specimen.

APPENDIX A
ACTIVITY CALCULATIONS

Standard State: Pure elements and compounds.

Chart⁴¹ reported Gibbs energies of solution for silicon in the Cr + Cr₃Si two-phase region for temperatures ranging from 1450 to 1700 K. From these data, the plot of $-\ln(a_{\text{Si}})$ versus 1000/T shown in Figure 40 was constructed, and a linear extrapolation to 1323 K allowed for the activity of silicon in this two-phase region to be obtained. For the assumption that Cr₃Si is a stoichiometric compound, the reaction

can be written where the Gibbs energy of formation of Cr₃Si and the activity of Si are now known, thus allowing the calculation of the activity of Cr in this two phase region.

Thus at 1323 K

$$a_{\underline{\text{Si}}} = 1.3 \times 10^{-4}$$

$$a_{\underline{\text{Cr}}} = 0.54$$

Similarly, using the Gibbs energies of formations provided by Eremenko²⁹ the activities for Cr and Si for all of the two-phase regions can be determined.

Two-phase region $\text{Cr}_3\text{Si} + \text{Cr}_5\text{Si}_3$:

$$a_{\underline{\text{Cr}}} = 0.12$$

and

$$a_{\underline{\text{Si}}} = 1.1 \times 10^{-2}$$

Two-phase region $\text{Cr}_5\text{Si}_3 + \text{CrSi}$:

$$a_{\underline{\text{Cr}}} = 2.9 \times 10^{-2}$$

and

$$a_{\underline{\text{Si}}} = 0.11$$

Two-phase region $\text{CrSi} + \text{CrSi}_2$:

$$a_{\underline{\text{Cr}}} = 2.2 \times 10^{-2}$$

and

$$a_{\underline{\text{Si}}} = 0.15$$

Two-phase region $\text{CrSi}_2 + \text{Si}$:

$$a_{\underline{\text{Cr}}} = 5.1 \times 10^{-4}$$

and the activity of Si approximates unity in this two-phase region.

Figure 40. Linear extrapolation of $-\ln(a_{\text{Si}})$ versus $1000/T$ calculated from Gibbs energies^{of solution} for Si^{41} .

APPENDIX B
3.5% NaCl AQUEOUS CORROSION DATA

Table 7. Linear polarization data for uncoated AISI 1018 steel tested in a 3.5% NaCl aqueous solution at room temperature.

Cathodic

<u>Time (min.)</u>	<u>ΔE (mV)</u>	<u>I_{app} (μA)</u>
0.0	-673	0.0
0.5	-675	-1.5
1.0	-678	-2.2
2.5	-680	-3.0
4.0	-682	-4.0
6.0	-684	-4.2

Anodic

<u>Time (min.)</u>	<u>ΔE (mV)</u>	<u>I_{app} (μA)</u>
0.0	-675	0.0
0.5	-674	1.0
1.5	-672	2.2
2.5	-670	4.0
3.5	-668	5.5
4.5	-666	6.5

Table 8. Linear polarization data for coated AISI 1018 steel (surface concentration Fe-9wt%Cr-3Si) tested in a 3.5% NaCl aqueous solution at room temperature.

Cathodic

<u>Time (min.)</u>	<u>ΔE (mV)</u>	<u>I_{app} (μA)</u>
0.0	-618	0.0
1.0	-620	0.0
2.0	-622	-0.5
3.0	-624	-1.0
4.0	-626	-2.0
5.0	-628	-2.5

Anodic

<u>Time (min.)</u>	<u>ΔE (mV)</u>	<u>I_{app} (μA)</u>
0.0	-620	0.0
1.0	-618	1.0
2.0	-616	2.0
3.0	-614	3.0
4.0	-612	4.2
5.0	-610	5.8

Table 9. Linear polarization data for coated AISI 1018 steel (surface concentration Fe-30wt%Cr-3Si) tested in a 3.5% NaCl aqueous solution at room temperature.

Cathodic

<u>Time (min.)</u>	<u>ΔE (mV)</u>	<u>I_{app} (μA)</u>
0.0	-464	0.0
1.0	-466	0.0
2.0	-468	0.0
3.0	-470	0.0
4.0	-472	-0.1
5.0	-474	-0.1

Anodic

<u>Time (min.)</u>	<u>ΔE (mV)</u>	<u>I_{app} (μA)</u>
0.0	-466	0.0
1.0	-464	0.0
2.0	-462	0.1
3.0	-460	0.2
4.0	-458	0.2
5.0	-456	0.2

Table 10. Tafel polarization data for uncoated AISI 1018 steel tested in a 3.5% NaCl aqueous solution at room temperature.

Cathodic

<u>Time (min.)</u>	<u>ΔE (mV)</u>	<u>I_{app} (μA)</u>
0.0	-676	0.0
1.0	-690	-8.0
3.0	-700	-10.0
4.0	-710	-12.0
5.0	-720	-14.0
6.0	-730	-16.0
7.0	-740	-17.8
8.0	-750	-19.0
9.0	-760	-20.0
11.0	-770	-21.0
12.0	-780	-21.8
13.0	-790	-22.2
14.0	-800	-22.8
15.0	-810	-23.8
16.0	-820	-24.0
17.0	-830	-25.0
18.0	-840	-25.6
19.0	-850	-26.0
20.0	-860	-27.0
21.0	-870	-27.8

Anodic

<u>Time (min.)</u>	<u>ΔE (mV)</u>	<u>I_{app} (μA)</u>
0.0	-673	0.0
1.0	-660	10.0
2.0	-650	20.0
3.0	-640	32.0
4.0	-630	49.0
5.0	-620	70.0
6.0	-610	100.0
7.0	-600	140.0
8.0	-590	195.0
9.0	-580	260.0
10.0	-570	360.0
11.0	-560	480.0
12.0	-550	630.0
13.0	-540	845.0

Table 11. Tafel polarization data for coated AISI 1018 steel (surface concentration Fe-9wt%Cr-3Si) tested in a 3.5% NaCl aqueous solution at room temperature.

Cathodic

<u>Time (min.)</u>	<u>ΔE (mV)</u>	<u>I_{app} (μA)</u>
0.0	-626	0.0
1.0	-640	-4.2
2.0	-650	-7.0
3.0	-660	-9.0
4.0	-670	-10.2
5.0	-680	-14.0
6.0	-690	-14.0
7.0	-700	-15.0
8.0	-710	-16.0
9.0	-720	-17.0
10.0	-730	-18.0
11.0	-740	-18.2
12.0	-750	-20.2
13.0	-760	-21.0
14.0	-770	-21.0
15.0	-780	-24.1
16.0	-790	-23.0
17.0	-800	-22.0
18.0	-810	-22.0
19.0	-820	-22.0

Table 11. (continued)

Anodic

<u>Time (min.)</u>	<u>ΔE (mV)</u>	<u>I_{app} (uA)</u>
0.0	-595	0.0
1.0	-580	6.2
2.0	-570	13.5
3.0	-560	17.0
4.0	-550	24.0
5.0	-540	31.0
6.0	-530	40.0
7.0	-520	52.0
8.0	-510	68.0
9.0	-500	90.0
10.0	-490	120.0
11.0	-480	158.0
12.0	-470	205.0
13.0	-460	265.0
14.0	-450	340.0
15.0	-440	440.0
16.0	-430	600.0
17.0	-420	770.0
18.0	-410	1080.0
19.0	-400	1500.0
20.0	-390	2000.0

Table 12. Tafel polarization data for coated AISI 1018 steel (surface concentration Fe-30wt%Cr-3Si) tested in a 3.5% NaCl aqueous solution at room temperature.

Cathodic

<u>Time (min.)</u>	<u>ΔE (mV)</u>	<u>I_{app} (uA)</u>
0.0	-462	0.0
1.0	-470	0.0
2.0	-480	-0.1
3.0	-490	-1.0
4.0	-500	-1.8
5.0	-510	-2.0
6.0	-520	-2.1
7.0	-530	-2.7
8.0	-540	-3.2
9.0	-550	-3.9
10.0	-560	-4.0
11.0	-570	-4.2
12.0	-580	-4.8
13.0	-590	-5.4
14.0	-600	-6.0
15.0	-610	-6.2
16.0	-620	-6.8
17.0	-630	-7.2
18.0	-640	-7.8
19.0	-650	-8.0
20.0	-660	-8.1

Table 12. (continued)

Anodic

<u>Time (min.)</u>	<u>ΔE (mV)</u>	<u>I_{app} (μA)</u>
0.0	-455	0.0
1.0	-445	0.8
2.0	-435	1.8
3.0	-425	2.0
4.0	-415	2.2
5.0	-405	2.5
6.0	-395	3.0
7.0	-385	3.9
8.0	-375	4.1
9.0	-365	5.0
10.0	-355	5.8
11.0	-345	6.0
12.0	-335	6.8
13.0	-325	8.0
14.0	-315	8.0
15.0	-305	9.5
16.0	-295	14.0
17.0	-285	15.0
18.0	-275	27.0
19.0	-265	50.0
20.0	-255	120.0
21.0	-245	280.0
22.0	-235	600.0
23.0	-225	1100.0
24.0	-215	1600.0

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