



Pack Cementation Diffusion Coatings For Iron-Base Alloys

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PACK CEMENTATION DIFFUSION COATINGS FOR Fe-BASE ALLOYS: FINAL REPORT

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ABSTRACT

With the aid of computer-assisted calculations of the equilibrium vapor pressures in halide-activated cementation packs, processing conditions have been identified and experimentally verified for the codeposition of two or more alloying elements in a diffusion coating on a variety of steels. The Cr-Si ferrite layers have proven to be very resistant to high temperature cyclic oxidation and to pitting in aqueous solutions. The process has been patented, and is being transferred for industrial application, e.g. for water walls of utility boilers, etc. In the proposed extension of this project, the use of mixed pure metal powders in the pack will be extended to achieve similar ferrite Fe-Cr-Al coatings with excellent oxidation resistance, with the eventual transfer of the technology to industry.

In other recent studies, Ni-base alloy rods were aluminized by the halide-activated pack cementation process to bring their average composition to that for the ORNL-developed Ni₃Al, for use as a welding rod. A similar effort to develop a welding rod for the ORNL Fe₃Al alloy did not yield reproducible coating compositions or growth kinetics. The continued effort to produce Duriron-type (Fe-18Si-5Cr) coatings on steels was not successful. Literature for the intrinsic diffusion coefficients suggests that this task cannot be achieved.

INTRODUCTION

Carbon steels or low alloy steels have served as the workhorse material in the construction of utility boilers, heat exchangers and other power generation installations. However, these steels suffer from corrosion attack in

the forms of oxidation, sulfidation, and deposition corrosion in these applications. In particular, sulfidation, resulting from the presence of sulfur in low grade fuel, shortens the service life of these structures considerably. High alloy steels (e.g., stainless steels and nickel-base alloys) may survive in these environments, but the associated cost and susceptibility to stress corrosion cracking (SCC) have made these alloys unlikely choices for the major materials of construction for these applications.

Appropriate coatings, applied to carbon or low alloys steels, have long been sought as a means to combat these corrosion problems. Physical vapor deposition, chemical vapor deposition, thermal spray and plasma spray have various advantages and disadvantages. The associated high costs for low-pressure vapor deposition equipment limits its acceptability for large scale application. Spraying methods constitute a line-of-sight technology, which makes them impractical to protect certain geometries, such as the inside walls of heat exchanger tubing. Also, some spray coatings suffer oxidation, high porosity and poor adhesion to the substrate material, leaving them particularly vulnerable to corrosion attack.

A variety of pack cementation diffusion coatings have been used in the aerospace, chemical, and utility industries for about 75 years. These coatings can be inexpensively produced, they are strongly adherent to the substrate, and they are rather versatile in terms of enriching an alloying element at the surface. In fact, the long history of these diffusion coatings gives them a psychological handicap, as they may not be considered "high tech" or "trendy", and decades of occasional inadequate or shoddy application by various industrial shops may have created an unfavorable general reputation for the process. Furthermore, in the past, the pack cementation process was only practiced to add a single element to the substrate; this restriction has limited the ability of the coating to protect the workpiece from a variety of corrosion conditions.

Often, the best corrosion protection is provided by an enrichment at the surface of two or more beneficial alloying elements, which can produce a very favorable "synergistic effect" in corrosion protection. Sequential diffusion coating of two or more elements on carbon steels and low alloy steels can be done in industry; however, the additional (labor-intensive) furnace runs and the resulting irregular concentration profiles do not make this practice attractive. So to modernize and improve the practice of halide-activated pack cementation coatings, a means was needed to codeposit two or more elements

simultaneously in the proper concentrations. But such a process faces an inherent difficulty analogous to the electroplating of an alloy, where different elements generally exhibit greatly differing standard half-cell reduction potentials. As shown in our research, the analogous difficulty in codepositing elements by pack cementation is the greatly differing standard Gibbs energies of formation of the various volatile halides for the different metallic components of interest.

The principal goal of the DOE-sponsored research of this project was to provide a much better scientific understanding for the halide-activated pack cementation process, which could lead to the controlled coating of various steels with two or more alloying elements in one thermal process step. As detailed in the following, this approach has achieved significant success and has led to the development of a number of different coatings with superior high-temperature and aqueous corrosion resistance in laboratory (and some industrial) testing. Some such processing successes are currently being transferred for application by industry, and others are under consideration.

PREVIOUS PROCESSING PROGRESS

Research conducted at The Ohio State University (OSU) over the past 10 years has focused on producing pack cementation diffusion coatings with the deposition of multiple alloying elements during a single furnace run. This "codeposition" has been successful in depositing Cr-Al, Cr-Si, Cr-Si-V, Cr-Si-Ce coatings on low-carbon steels, Cr-Al on several different austenitic steels, Al and Al-B to transform Fe_3Al to FeAl , and Cr-Al-RE (RE=reactive element) coatings on nickel-base superalloys (Navy support). Also codeposition has been achieved for the formation of B-modified and Ge-doped silicide coatings on Ti, Ti-Al-Nb, and Nb-Al-Ti alloys, and on Mo (Air Force and Navy support). Through the latter studies, a simple means for the absolute avoidance of low-temperature (500°C) "peeting" of MoSi_2 was discovered. These successes are listed here only briefly, because they have been reported in detail in previous DOE reports, and have been published in the open scientific literature. Furthermore, a US patent No. 5364659 was recently granted to M. A. Harper and R. A. Rapp at OSU for "Codeposition of Chromium- and Silicon-Diffusion Coatings in Fe-Base Alloys Using Pack Cementation". Babcock and Wilcox (B & W) cooperated with OSU in submitting the patent application, and is

presently arbitrating an exclusive license for this technology.

RECENT PROCESSING PROGRESS

The early stages of this codeposition technology have relied on the use of previously manufactured masteralloy powders which are relatively expensive. By the use of a masteralloy in the pack, the thermodynamic activity of the normally favored element could be reduced, such that with the proper choice of halide activator salt and process temperature, codeposition, e.g. of Cr-Si or Cr-Al into steels, became possible. But more recently, this DOE-sponsored project has focused its effort in reducing the material cost, optimizing the diffusion process, understanding further the high temperature gas chemistry, and interacting with industry. For example: 1) The "common component effect" has been elucidated, which provides a basis for an effective choice of the halide activators in the cementation pack. 2) The costly masteralloys used in initial pack chemistries have been eliminated; instead, inexpensive elemental powders are currently used in most cementation packs. These should also be better suited to rejuvenation in an industrial process. 3) By optimizing the activator(s), the coating time has been shortened to reduce the required energy input for the coating process, the extent of decarburization of the steel has been minimized, and the formation of the undesirable blocking chromium carbide layer on carbon-containing steels has been avoided. 4) Numerous trial runs have been conducted in response to inquiries from industry. 5) Extensive high-temperature and aqueous corrosion tests have been conducted in the laboratory. 6) The important results (except those withheld for patent reasons) have been submitted for publication in the open literature. In the following, some brief accounts are given of recent progress (last two years) for the various project tasks.

Thermodynamic Analyses; the "Common Component Effect"

After the introduction by Mark Harper of the combined use of a chloride plus a fluoride salt to achieve codeposition of Cr and Si into steels, a more general analysis and understanding of the use of dual activators seemed to be needed. As part of a Senior Project, Miss Ning He and Dr. Ge Wang cooperated to run numerous different SOLGASMIX-type computer-assisted

calculations of the equilibrium partial pressures for packs containing pure Cr and pure Si powders with various combinations of activators: single salt, fluoride and chloride salts with a common cation, and fluoride and chloride salts with different cations. Table I shows the results of these calculations. While Table I is rather detailed, so that close inspection is required, the conditions (activators) suitable for the codeposition of Cr and Si have been identified in this way, and these predictions have been verified experimentally.

Figure 1 presents a schematic illustration of the processing scheme required in codepositing Cr + Si so that an enriched ferrite surface layer can be grown without the formation of a blocking Cr carbide surface layer. In short, the ferrite-stabilizing Si must be transported to the surface at a low temperature, e.g. 830°C, such that the carbon in the steel is rejected into the austenite core, before the CrCl_2 vapors reach a sufficient vapor pressure to form Cr_{23}C_6 at a higher temperature. Once the ferrite case has been initiated, the inward rejection of carbon in front of the growing ferrite permits the addition of Cr solute to the ferrite layer without carbide formation. A similar scheme is applicable for the codeposition of Cr + Al, which study is proposed for the extension of the existing project. The theory about the "common component effect" and its application to the codeposition of Cr-Si was presented as an invited talk at a Materials Chemistry Conference in Vienna, and the corresponding publication has been submitted to the journal High Temperature Science. In fact, the Cr-Si codeposition into steels has now been achieved by the use of pure powders of Cr and Si, instead of the earlier Cr-Si masteralloy technology, and this result is the subject of a second B & W - prepared submission to the US patent office. For this reason, the details of the pack composition and processing procedure are not presented here.

Aqueous Corrosion Resistance of Cr-Si-RE Coatings on Steels

As the subject for a recently completed MS thesis by Miss Endang Pangestuti, an Indonesian student whose University expenses were paid by the oil company which employs her, pack cementation coatings with compositions on the order of 35Cr-4Si (and with or without a small concentration of either cerium or vanadium) were tested by scanning potentiometry in laboratory-simulated seawater. The coatings were deposited onto both 304 and 316 austenitic steels, as well as interstitial-free and low-carbon steels. Again the

pack contained a mixture of elemental Cr and Si powders to produce the Cr-Si, Cr-Si-Ce and Cr-Si-V coatings. Figure 2 shows anodic polarization curves for the coatings tested in a 0.6M NaCl/0.1M Na₂SO₄ solution at room temperature. The additions of Ce and V to the Cr-Si coatings were found to provide important improvements in the pitting resistance, i.e. extension of the passive plateau to higher oxidizing potentials and reduction of the passive current density. Even for applications in high temperature fossil fuel systems, e.g. coal gasification units, aqueous corrosion resistance is important in resisting attack by hydrolyzed deposits during downtime. The results of this MS thesis research have been submitted for publication in the journal Corrosion.

Pack Cementation Coatings to Form Welding Rods for NiAl and FeAl

This was the MS thesis topic for the Chris McVay. Because of their inadequate fabricability to accomplish wire drawing, the structural alloys Ni₃Al and Fe₃Al developed principally at ORNL required the creation of welding rods by another means. In fact, these intermetallic phases each also contain a number of other alloying elements to optimize their properties. In this research, an attempt was made to aluminize wires of the Ni-base and Fe-base alloy compositions corresponding to the ORNL-developed Ni₃Al and Fe₃Al materials, except that the wires were low, or devoid, of Al. Then the goal was to deposit coatings sufficiently rich in Al so that the average compositions corresponded to those for the intermetallic phases. For the Ni-base alloy, an external coating of Ni₂Al₃ was grown. For this system, sets of conditions (pack composition, temperature, and times) were found to achieve the goal. Figure 3 presents the coating microstructure, and Fig. 4 shows the growth kinetics to achieve the desired average composition for the Ni₃Al phase. As a most favorable aspect for the growth of this coating, the Ni₃Al grew dominantly by the inward diffusion of Al, so that the resulting layer did not entrap pack particles. A paper describing this research has been submitted for publication to Scripta Met. Mater.

The analogous problem for coating the Fe-base alloy was more difficult, as the required Fe₂Al₃ coating phase grew by dominant outward diffusion of Fe. In that case, a coating free of pack entrapment can only be grown by an "above pack" arrangement. For the available time and resources, a sufficiently

controlled coating process could not be achieved. Chris McVay has completed his MS degree and now works for Allegheny-Ludlum.

The Silicide Coating of Steels to the Fe₃Si (Duriron) Composition

The Fe₃Si composition, especially when alloyed with about 4-6 wt.% Cr, constitutes the metallic composition with the best resistance to inorganic acids such as nitric and sulfuric acids. The corresponding commercial alloy Duriron is brittle and can only be fabricated by casting. Obviously, a Fe₃Si diffusion coating on a steel with more ductility and toughness would find numerous important applications, an opportunity that has been obvious to researchers around the world for at least 50 years. However, for reasons that have not been obvious previously, past research has not been able to grow a dense diffusion coating of Fe₃Si on iron. This search for the "Holy Grail" of coatings became the MS thesis for Ted Cruise. Although considerable progress was made, the desired coating process was not achieved. However, the experiments clearly pointed out that significant coating growth occurred by outward Fe diffusion, so that pack pickup was unavoidable unless an "above pack" arrangement was used. According to the limited literature on interdiffusion in the Fe-Si system, the magnitudes for the intrinsic diffusion coefficients for Fe and for Si cross in the range of composition from pure Fe to Fe₃Si, as shown in Fig. 5. Since in the diffusional growth of Fe₃Si on Fe, vacancies diffuse in the same direction as the component with the lower intrinsic diffusion coefficient, in the Fe-Si system, the vacancies in growing Fe₃Si flow from opposite directions to the Fe-10Si composition, a circumstance which inherently generates voids and a porous coating. The experiments of Ted Cruise could not uncover any halide activator which would avoid the inherent porosity. However, siliciding with some fluoride activators did create a Si surface composition higher than Fe₃Si, a previously unattainable result. At this time, there is considerable doubt that the growth of an Fe₃Si layer on steels can ever be achieved, and continuation of this task is not proposed.

PROJECT HISTORY

This project was initiated in November 1987, and through February 28, 1995, a total of \$661,326 has been budgeted for this research. The project has

supported the research of 6 MS students (Ed Naylor, Denis O'Connell, Fred Geib, Mingang Zhu, Ted Cruise and Chris McVay), 2 PhD students (David Miller and Mark Harper), and 4 Post-Doc researchers (Patrick Choquet, Ge Wang, Xiao Ru Wan, and Yrong He). A list of publications in the open literature follows; many presentations at many conferences were made, but such an accounting list has not been made. In addition, one patent (US 5364659) has been granted, and one other is pending, and one further OSU disclosure has been submitted.

Project Publications

D. M. Miller, S.C. Kung, S.D. Scarberry and R.A. Rapp, "Simultaneous Chromizing-Aluminizing Coating of Austenitic Stainless Steels", *Oxid. Metals*, **29**, (1988) 239; *ibid*, Thermochemistry of Alloys NATO-ASI Series, C286, H. Brodowsky and H.J. Schaller, Eds., (1987) 547.

R. A. Rapp, "Pack Cementation Coating of Steel for High Temperature Applications", paper 131, Corrosion 88, NACE.

V. A. Ravi, P. Choquet, and R.A. Rapp, "Thermodynamics of Simultaneous Chromizing-Aluminizing of Alloys in Halide-Activated Cementation Packs", MRS International Meeting on Advanced Materials, Vol. 4. Tokyo (1989), pp. 483-500.

V. A. Ravi, P. Choquet and R. A. Rapp, "Chromizing-Aluminizing Coating of Ni- and Fe-Base Alloys by the Pack Cementation Technique", Oxidation of High Temperature Intermetallics, T. Grobstein and J. Doychak, eds., TMS, Warrendale, PA, pp.127-145.

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.

P.A. Choquet, E.R. Naylor and R.A. Rapp, "Simultaneous Chromizing and Aluminizing of Iron-Base Alloys", Materials Science and Engineering, A121, (1989) pp. 413-418.

R.A. Rapp, "Pack Cementation Coatings of Steels for Fossil Fuel Environments", Corrosion 1989, NACE, paper #532.

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, 1990.

M.A. Harper and R. A. Rapp, "Chromized-Siliconized Diffusion Coatings for Iron-Base Alloys by Pack Cementation", Paper #66, Corrosion 91, NACE 1991; ibid Materials Performance, Sept. (1991) pp.41-44.

M.A. Harper and R. A. Rapp, "Chromized-Siliconized Pack Cementation Diffusion Coatings for Heat-Resistant Alloys", in Heat-Resistant Materials, K. Natesan and D.J. Tilack, Eds., ASM Internat., (1991), pp. 379-86.

F.D. Geib and R.A. Rapp, "Diffusion Coatings for Iron Aluminide Fe₃Al by Halide-Activated Pack Cementation", Processing and Manufacturing of Advanced Materials for High Temperature Applications, V.A. Ravi and T.S. Srivatsan, Eds., TMS Warrendale, PA, pp. 347-60.

R.A. Rapp, "Fundamental Aspects of High-Temperature Corrosion", J. Phys. IV, Colloque C9, 3, Dec. (1993) pp. 1-15.

M.A. Harper and R.A. Rapp, "Codeposited Chromium and Silicon Diffusion Coatings for Fe-Base Alloys Via Pack Cementation", Oxid. Metals, Vol. 42, Nos. 3/4, (1994) pp. 303-333.

R.A. Rapp, "The Codeposition of Elements in Diffusion Coatings by the Pack Cementation Method", Proceedings of International Workshop on Gasifiers, Petten, Netherlands, June 1993; Materials at High Temperatures, 11, (1993) pp. 181-4.

F.D. Geib and R.A. Rapp, "Simultaneous Chromizing-Aluminizing Coating of Low Alloy Steels by a Halide-Activated Pack Cementation Process", Oxid. Metals, 40, (1993) pp.213-28.

X. Wan, G. Wang, and R.A. Rapp, "Resistance to Aqueous Corrosion of Steels Protected by a Cr-Si Diffusion Coating", Proceedings of International Corrosion Congress, Sept. 1993, Vol. 1, pp. 353-69, NACE, Houston, TX..

N. He, G. Wang, and R.A. Rapp, "The Common Component Effect in Multiphase, Multicomponent Equilibria", submitted for publication to High Temperature Science, (1994).

C. McVay and R.A. Rapp, "Diffusion Aluminizing Coatings to Produce Ni₃Al Alloy Welding Rods", submitted for publication to Scripta Met & Mater. Oct. (1994).

E. Pangestuti, G. Wang, and R.A. Rapp, "Aqueous Corrosion Resistance of Cr-Si Diffusion Coatings", submitted for publication to Corrosion.

HONORS AND AWARDS

During this project, a number of Honors and Awards were received by project participants:

Mark Harper:

TMS Graduate Student Paper Award

BFGoodrich Collegiate Inventor's Award (one of 3 in USA), 1992

Fulbright Scholarship to NS Wales, Australia 1992

Morris Cohen Outstanding Graduate Student Award of Corrosion Division of the Electrochemical Society, 1992

SAMPE Outstanding Graduate Student Award, 1991

Robert A. Rapp:

Fellow, The Electrochemical Soc. 1993

Fellow, NACE International, 1994

Distinguished Engineering Alumnus, Purdue University, 1988

National Academy of Engineering 1988

University Professor, The Ohio State University, 1989

Outstanding Achievement Award, High Temperature Materials Div., The Electrochemical Soc., (1990)

Membe d'Honneur, Societe Francaise de Metallurgie et de Materiaux, 1990

Acta/Scripta Metallurgica Lecturer, 1991-93

Lumley Research Award, OSU College of Engineering 1991

BFGoodrich Collegiate Inventor's Awards (one of three annual awards in USA), with student Robert Bianco, 1991; with student Mark Harper, 1992

Ulrick R. Evans Award, British Corrosion Institute, 1992

Chevalier dans l'ordre des Palmes academiques, Ministere de l'Education et de la Culture Francaise, 1993

PROPOSED RESEARCH

TASK 1: The use of elemental Cr and Al powders to produce Cr-Al coatings on carbon-containing steels, to thereby gain their excellent oxidation or sulfidation behavior, has only recently begun. The growth of very protective coatings using Cr-Al masteralloys was achieved earlier in the project by Fred Geib. More recently, based on the success in the codeposition of Cr-Si using pure metal powders, some preliminary coatings for steel using pure Cr and pure Al powders have been demonstrated. As shown in Fig. 6, the cyclic oxidation results for IF-iron coated by Cr-Al-Ce codeposition show that a proper 20Cr-4Al coating is superior in cyclic oxidation resistance to commercial Kanthal steel at 900C. In environments where high temperature oxidation/sulfidation corrosion is important, Al-containing coatings have a very distinctive advantage over other coating compositions, as a very protective Al_2O_3 film isolates sulfur from the substrate. Figure 7 presents the cyclic oxidation kinetics for other Cr-Al coatings at 700°C. (Readers should note the scaling factors for the ordinate and abscissa.) The coated steels were hardly tarnished after 2200 1-hr cycles in air at 700°C. However, these coatings have not been carefully characterized yet, nor is the experimental window for the process well known. Testing in a hot corrosion environment and in industrial reducing (carburizing/sulfiding) gases is required.

Therefore, as research proposed for the next two years, we will develop an optimal cementation pack for the codeposition of Cr-Al with following characteristics:

- 1) a pack composition using elemental Cr and Al powders
- 2) a pack with an addition of a reactive element-containing compound
- 3) a pack with the optimum choice of fluoride-chloride activator(s).

We will identify a thermal treatment to produce the RE-doped Cr-Al coating with the aforementioned pack composition, this process will produce a surface composition at least comparable to that of T406 stainless steels, i.e., >13 %Cr and >3%Al. This composition is known to provide excellent high-temperature

oxidation resistance and adequate sulfidation resistance to 850C. At the end of this project, OSU will provide the necessary assistance to transfer the technology to an industrial pack cementation coating shop. Discussions toward this goal have already commenced with ABB.

TASK 2: At the end of the this project period, we deposited preliminary Ge-doped silicide diffusion coatings for the ORNL-developed Cr-Nb alloy. From a mixture of pure Si and Ge powders and the NaF activator, at a temperature of 1050°C, an inward grown CrSi₂-base coating was produced on the alloy. However, the preliminary runs did not achieve sufficient Ge solute in the CrSi₂, so that excellent oxidation resistance cannot be expected. Oxidation testing by Dr. P. Tortorelli at ORNL is currently underway. From our considerable experience in siliciding pure Ti, Mo, Ti-Al-Nb, and Nb-Al-Ti alloys, the necessary process variations to improve the coating on the Cr-Nb alloy are apparent. In the extension of the project, this improved coating will be optimized and tested.

PERSONNEL and FACILITIES

After continued research in the development of the codeposition of elements by the pack cementation process for a decade, the research group of Professor Rapp is well equipped with high-temperature processing furnaces, the necessary computer software, the equipment required to establish the coating resistance to oxidizing and corroding environments, and the needed characterization instruments. For the proposed renewal period, Professor Rapp would advise the research of one Post-Doctoral researcher and one Graduate Assistant for a period of two years. The requisite budget estimate for \$238,843 for the period 3/1/95 to 2/28/97 has been submitted separately to DOE-ORNL.

Table I. Thermodynamic Calculation of Vapor Pressures in Cr-Si-Halide Systems

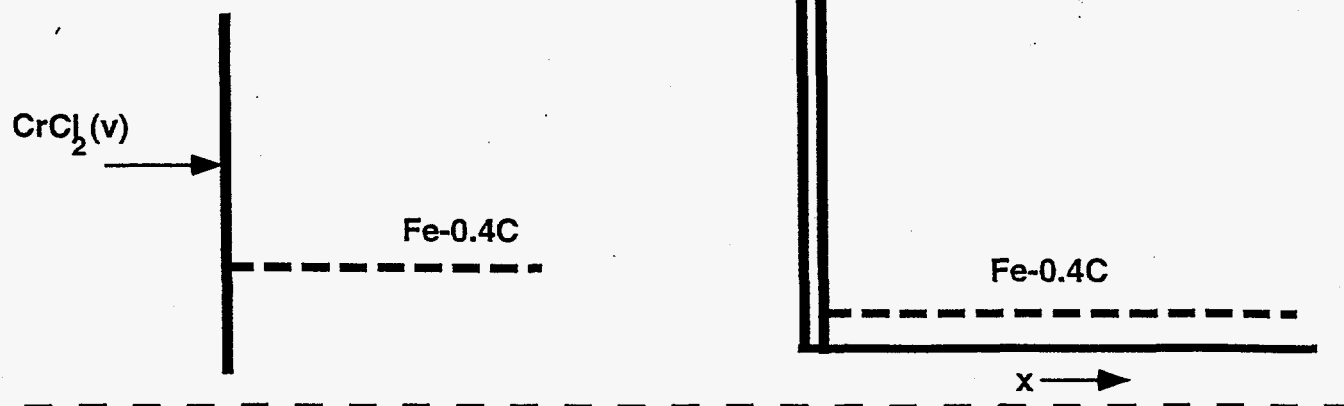
Single Salt	P(CrCl ₂)	P(SiF ₂)	P(SiCl ₂)	P(Cl)*	P(F)*	P(M1)**	P(M2)**	Comments
NaCl	3.66E-05		2.66E-05	1.20E-08		Na: 1.28E-4		
NaF		8.23E-05			2.76E-14	Na: 1.86E-2		High P(Na)
KCl	1.68E-05		1.22E-05	8.13E-09		K: 5.83E-5		
KF		1.08E-04			3.17E-14	K: 3.17E-2		High P(K)
MgCl ₂	9.34E-05		6.79E-05	1.92E-08		Mg: 1.49E-4		
MgF ₂		7.46E-06			8.28E-15	Mg: 1.01E-4		
CaCl ₂	7.28E-08		5.29E-08	5.36E-10		Ca: 1.44E-8		
CaF ₂		3.84E-08			5.96E-06	Ca: 3.75E-8		
Two Salts	P(CrCl ₂)	P(SiF ₂)	P(SiCl ₂)	P(Cl)	P(F)	P(M1)	P(M2)	Comments
Common Cations								
NaCl & NaF	1.65E-10	8.23E-05	1.20E-10	2.55E-11	2.76E-14	Na: 1.86E-2		P(CrCl ₂)
KCl & KF	5.66E-11	1.08E-04	4.11E-11	1.49E-11	3.17E-14	K: 3.17E-2		P(CrCl ₂)
MgCl ₂ & MgF ₂	8.24E-05	4.43E-06	6.00E-05	1.80E-08	6.40E-15	Mg: 1.7E-4		Minor Effect
CaCl ₂ & CaF ₂	4.66E-08	6.39E-08	4.39E-08	4.29E-10	7.69E-16	Ca: 2.25E-8		
Two Salts	P(CrCl ₂)	P(SiF ₂)	P(SiCl ₂)	P(Cl)	P(F)	P(M1)	P(M2)	Comments
Different Cations								
NaCl & KF	9.11E-11	2.00E-04	6.62E-11	1.90E-11	4.30E-14	Na:8.09e-2	K:2.34e-2	KF=0.1(mole)
NaCl & CaF ₂	4.17E-06	1.02E-05	3.03E-06	4.05E-09	9.72E-15	Na:3.78e-4	Ca:1.41e-10	
KCl & NaF	5.47E-10	1.00E-04	3.97E-10	4.64E-11	3.04E-14	Na:1.69e-2	K:1.02e-2	High P(K)
KCl & MgF ₂	4.75E-07	1.18E-05	3.45E-07	1.37E-09	1.04E-14	Mg:6.35e-5	K:3.46e-4	
KCl & CaF ₂	1.62E-06	6.95E-06	1.18E-06	2.53E-09	8.02E-15	Ca:2.07e-10	K:1.88e-4	
MgCl ₂ & NaF	8.48E-08	6.36E-03	6.16E-08	5.78E-10	5.80E-14	Mg:1.64e-1	Na:8.86e-3	
CaCl ₂ & NaF	6.46E-06	8.86E-06	4.70E-06	5.05E-09	9.05E-15	Ca:1.62e-10	Na:3.03e-4	
CaCl ₂ & KF	5.66E-11	1.08E-04	4.11E-11	1.49E-11	3.67E-14	Ca:1.33e-11	K:3.17e-2	KF=0.05(mole)
CaCl ₂ & MgF ₂	5.28E-06	7.24E-06	3.83E-06	4.56E-09	8.18E-15	Ca:1.99e-10	Mg:1.03e-4	

* P(Cl) and P(F) refer to the vapor pressures for the atomic vapors of the halogens, which exceed their molecular vapor pressures

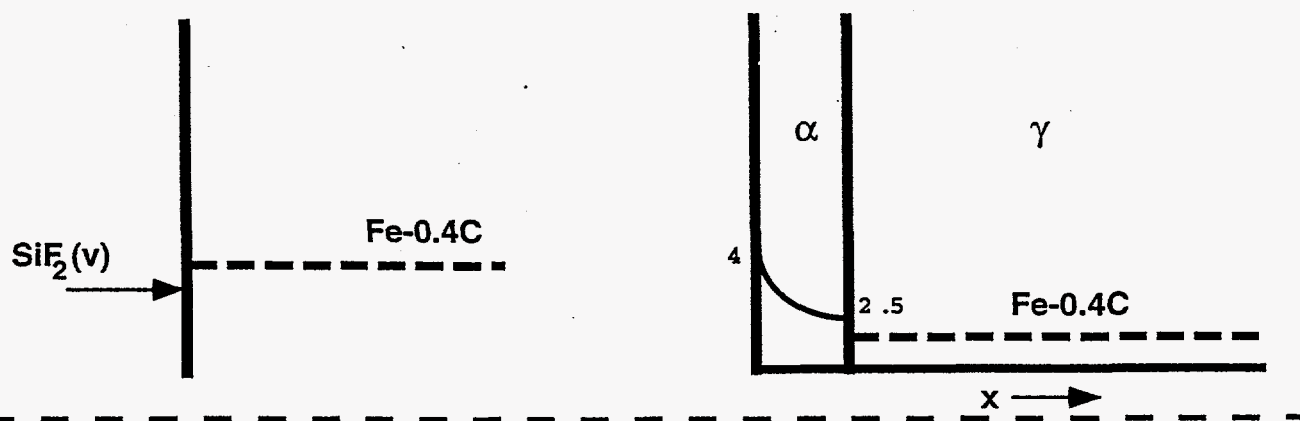
** P(M1) and P(M2) refer to the vapor pressures for the atomic vapors of the alkali or alkaline earth metals

Diffusion Coating of Steels

Chromizing



Siliconizing



Siliconizing Followed by Chromizing

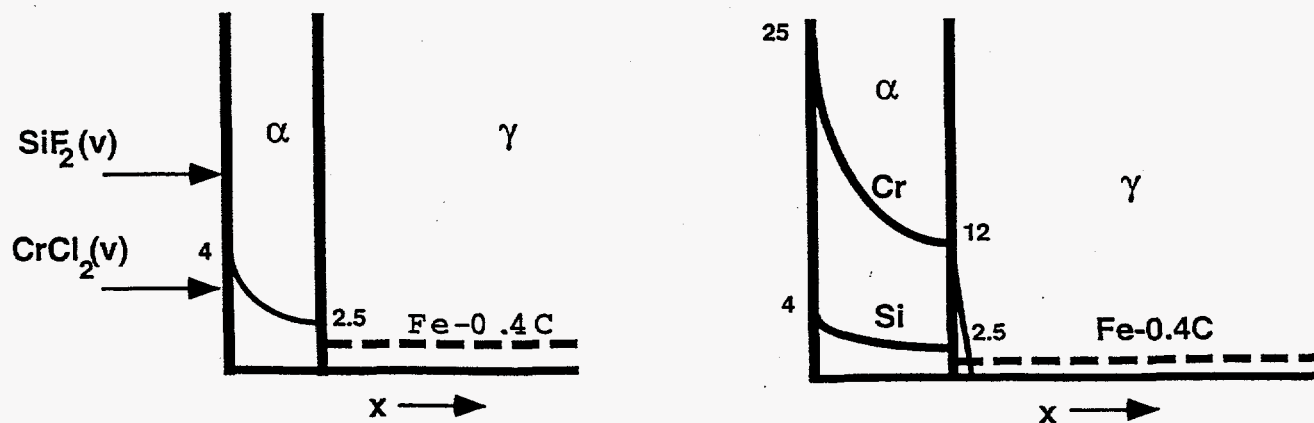


Fig. 1 Processing Scheme Illustrating Mode for Codeposition of Cr-Si (or Cr-Al) to Form a Ferrite Case without a Blocking Cr Carbide

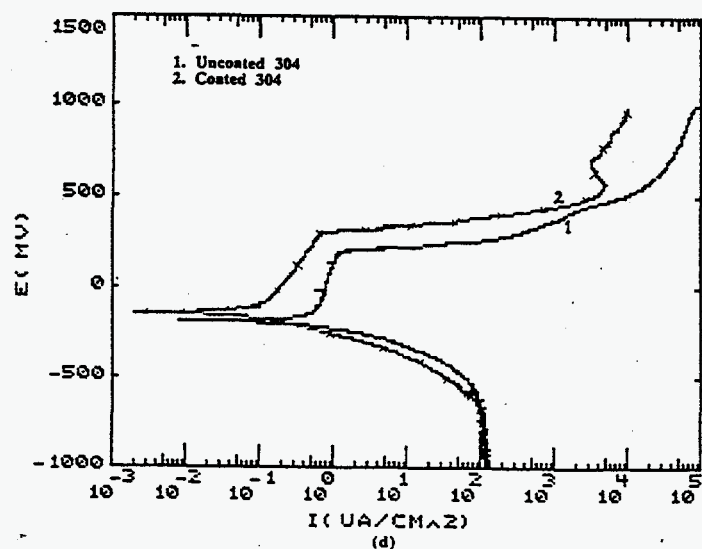
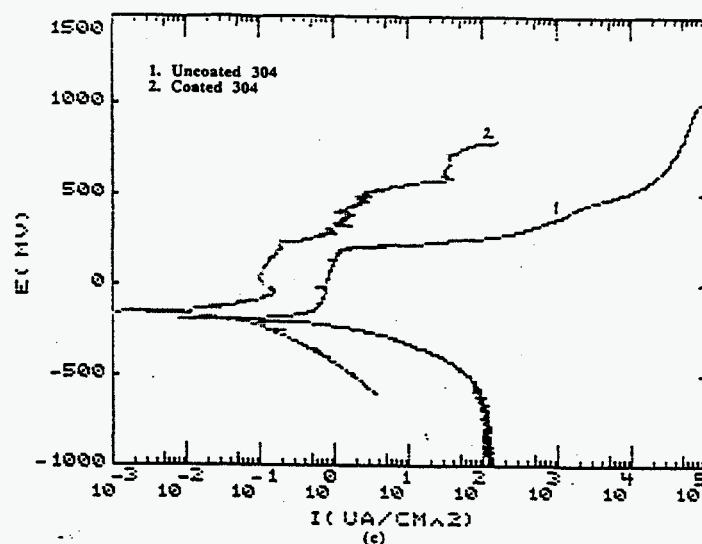


Figure 2. Potentiodynamic Curves for coated 304 coupons with the following surface compositions : (c) 48.9Cr - 3.67Si - 0.64V, and (d) 35.8Cr - 2.9Si with Ce added.

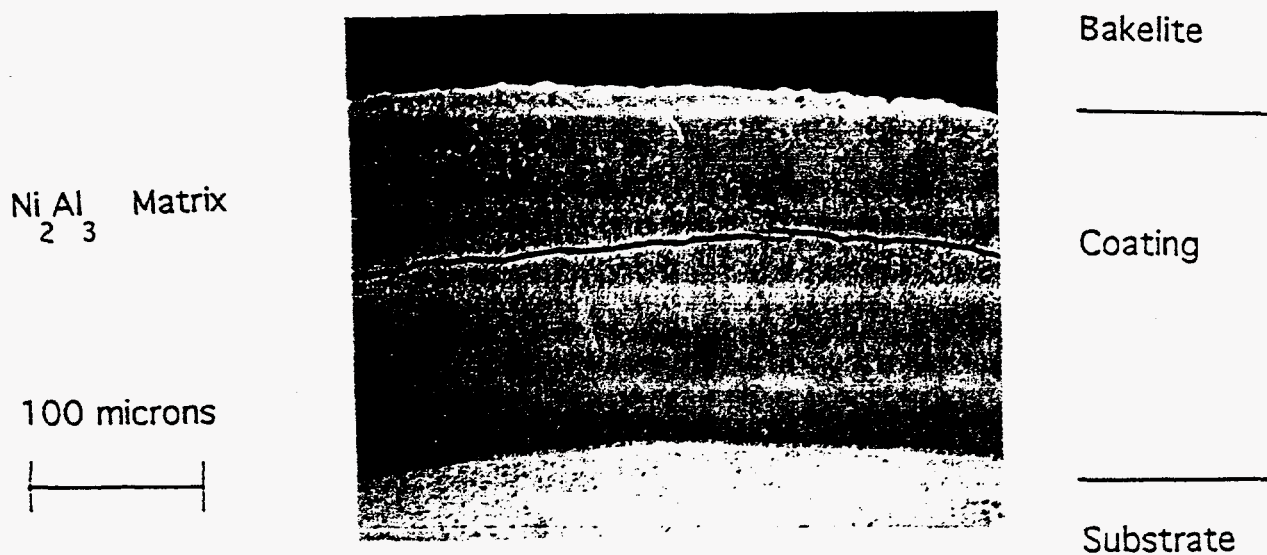


Figure 3 Coating Produced on Ni-base Alloy Substrate at 1000 °C for 7.8 hr. with 30-70 Ni-Al Source and AlF_3 Activator

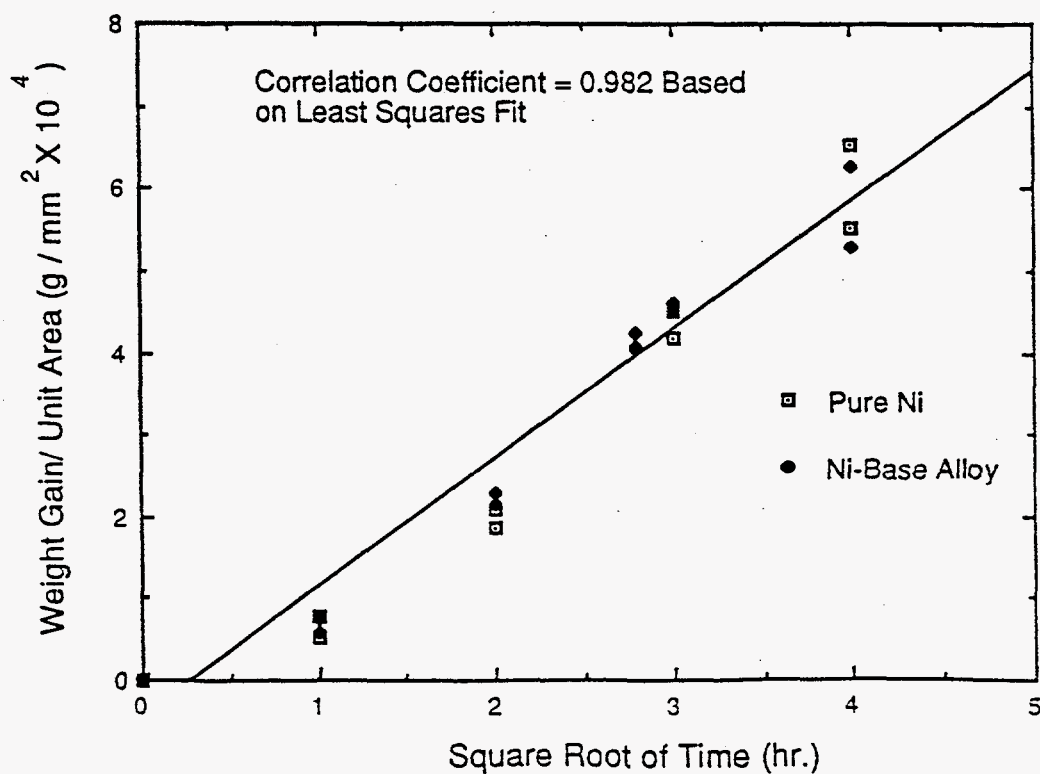


Figure 4 Weight Gain/ Unit Area vs. Square Root of Time for 30:70 Ni-Al, AlF_3 Packs

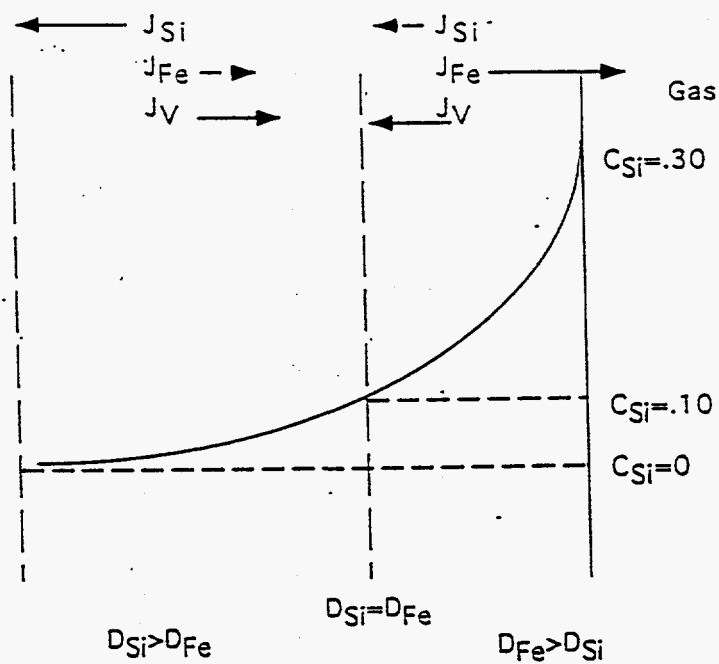
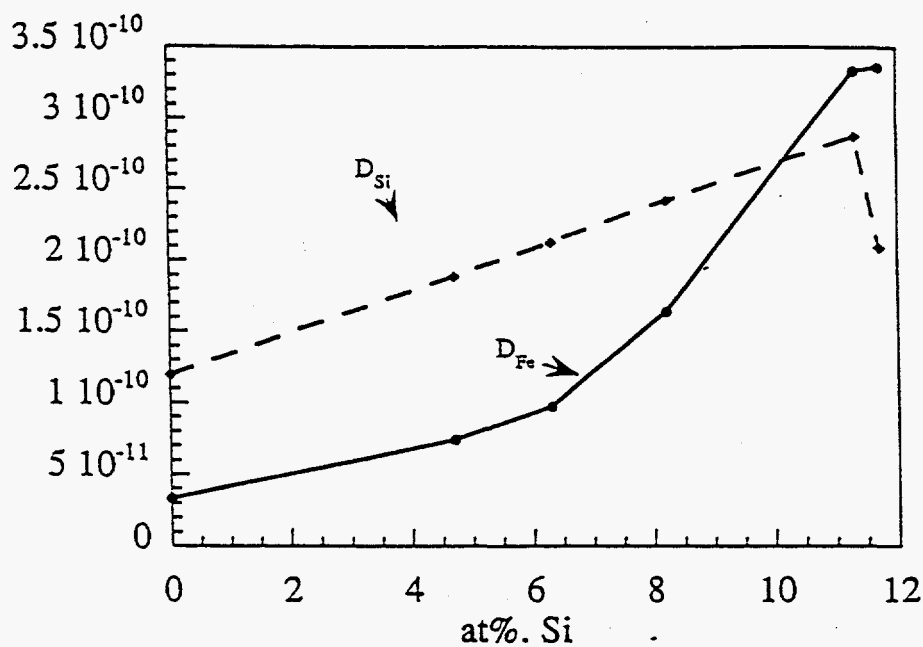


Figure 5 A. Plot in intrinsic diffusion coefficients for Fe and Si in Fe-Si alloys
 B. Corresponding schematic drawing of diffusion fluxes for the growth of an Fe_3Si layer on pure iron. Vacancies condense at $N_{Si} = 0.10$ composition.

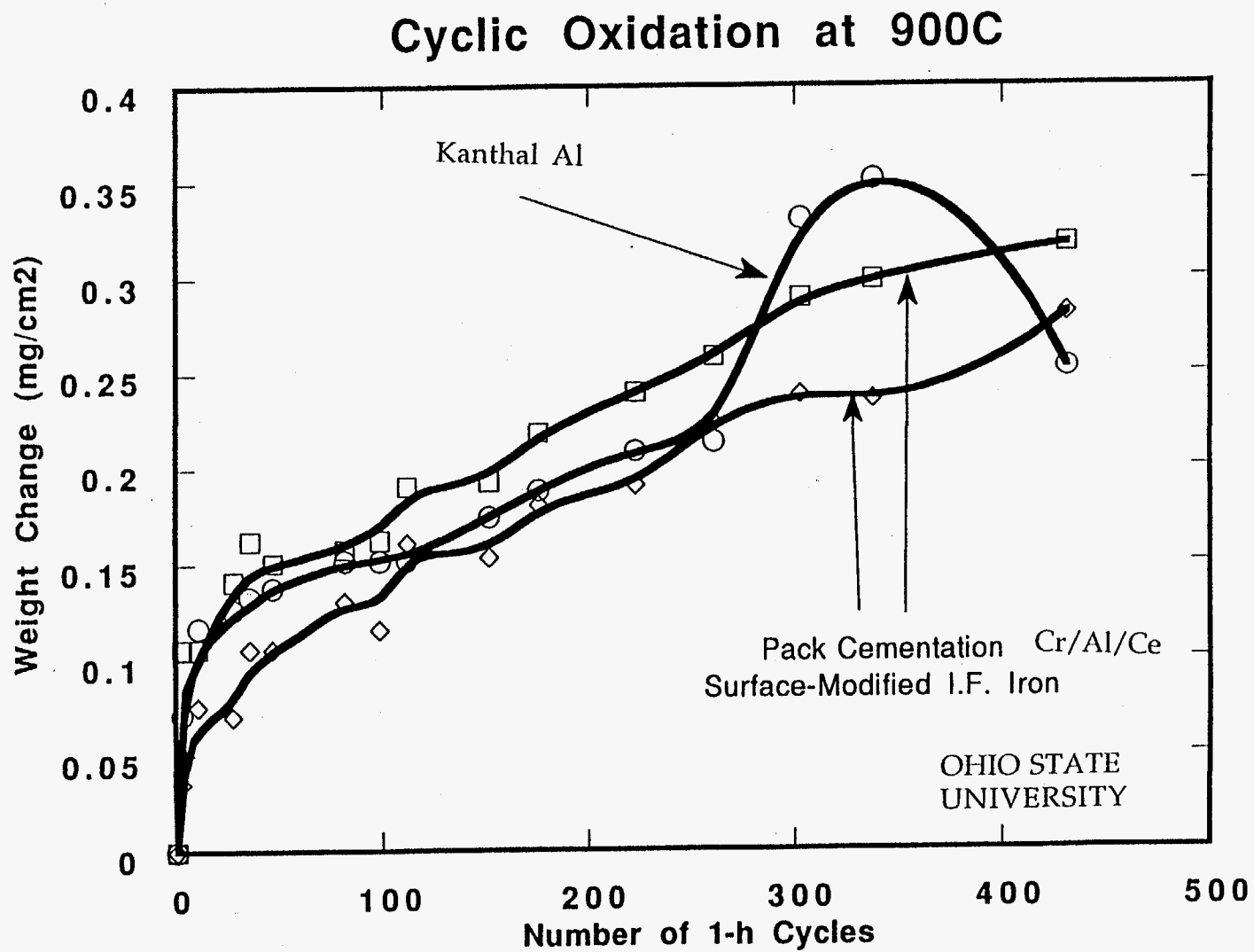


Fig 6. Cyclic oxidation of interstitial-free iron coated with Cr and Al at 900°C.
Kanthal Composition : Fe - 22.5 Cr - 5.5 Al

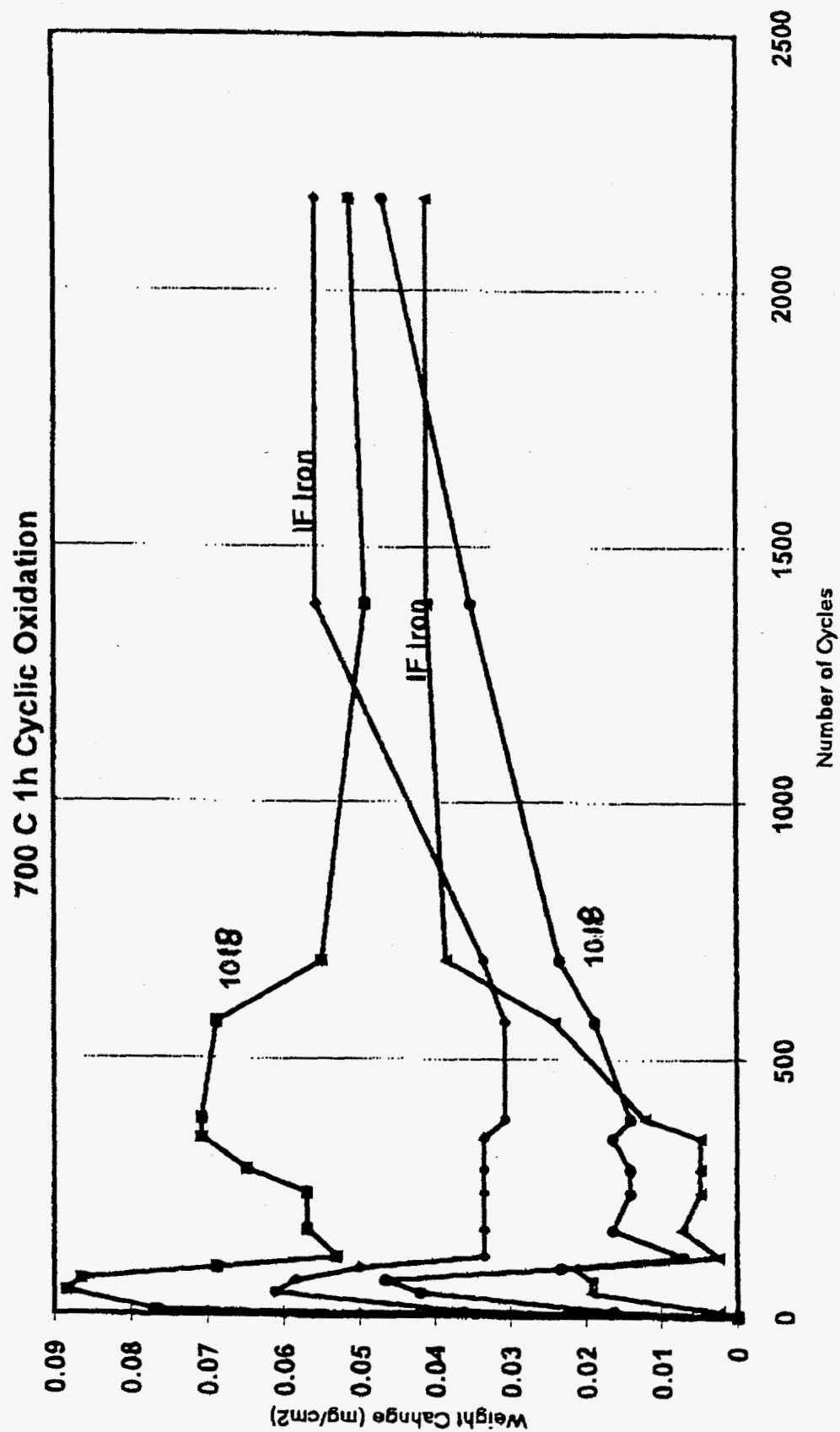


Fig. 7 Cyclic Oxidation Resistance in Air at 700°C for Steels Coated by Cr-Al Codeposition in a Cementation Pack Using Pure Metal Powders.

Appendix

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