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CODEPOSITION OF ELEMENTS IN DIFFUSION COATINGS BY THE HALIDE-ACTIVATED PACK CEMENTATION METHOD

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ABSTRACT

The codeposition of two or more elements in a halide-activated cementation pack is inherently difficult because of large differences in the thermodynamic stabilities for their volatile halides. However, through a computer-assisted analysis of the pack equilibria, combinations of suitable masteralloys and activator salts can be identified. Codeposition of Cr plus Al or Cr plus Si by pack cementation has yielded diffusion coatings with excellent resistance to high-temperature oxidation/corrosion for a wide range of alloy substrates.

INTRODUCTION

In general, for oxidation resistance, a ternary alloy using the interactive use of two oxidation-resistant elements is more effective than a simple binary alloy[1]. For example, when an alloy containing Fe-20wt%Cr-5Al is exposed to a high temperature oxidizing environment, initially a continuous adherent Cr_2O_3 scale is formed on the surface of the alloy. This Cr_2O_3 scale prevents the rapid oxidation of iron in the alloy and thereby eliminates the dissolution and inward diffusion of oxygen atoms which would otherwise cause the internal oxidation of Al. Escaping internal oxidation, the Al atoms diffuse to the Cr_2O_3/alloy interface and form an even slower growing, more protective Al_2O_3 scale at steady state. Actually the transient Cr_2O_3 and steady-state Al_2O_3 scales are quite thin, usually on the order of one to five microns or a few

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tenths of a mg/cm^2 oxygen-weight gain. Therefore, a pack cementation process which would deposit two elements simultaneously, producing a diffusion coating with a surface containing approximately 20-30wt%Cr and 4-6wt%Al or else 2-4wt%Si, should be very effective in protecting low-alloy substrates from corrosive environments at high temperature. These coatings should also provide protection from the accelerated corrosion that is seen when a fused salt deposit contacts the alloy surface (hot corrosion), as occurs for certain conditions in gas turbines and fossil fuel burning power plants. Furthermore, alumina and silica scales are known to be more resistant than chromia in gaseous environments containing mixed oxidants, e.g. carbon plus sulfur.

Pack cementation is an in-situ chemical vapor deposition batch process which has been used to generate corrosion- and wear-resistant coatings on inexpensive or otherwise inadequate substrates for over seventy-five years[2]. The traditional pack consists of four components: 1) the substrate or parts to be coated, 2) the masteralloy, i.e. powder of the element(s) to be deposited on the surface of the parts (e.g. Cr and/or Al, Cr and/or Si), 3) a halide salt activator (e.g. NaCl, NaF, NH_4Cl, etc.) and 4) a relatively inert filler powder (e.g. Al_2O_3 or SiO_2). The masteralloy, the halide salt activator, and the filler are mixed thoroughly, and the parts to be coated are buried in this mixture in a retort. The retort is heated to a high temperature (e.g. 1000-1150°C) while protected by an inert or reducing gas atmosphere. At the elevated temperature, the masteralloy reacts with the halide activator to produce volatile metal halides which diffuse through the gas phase of the porous pack to deposit into the substrate.

An aluminizing pack cementation process is practiced commercially for various steels and for the growth of NiAl on Ni-base superalloys for use in turbine engines[3]. Also, the surfaces of water wall panels in fossil fuel power plants are enriched with chromium (chromizing). Otherwise, both processes are used to provide coatings for chemical and petrochemical applications that must resist high temperature corrosive environments.

The engineering of pack chemistries to deposit simultaneously two or three elements has been achieved in the past several years[4-7]. A variety of alloys have been coated with Cr+Al (plain-carbon and low-alloy steels, 410, 304 and 316 SS, and Ni-base alloys) and Cr+Si (plain-carbon and low-alloy steels, 304, 409 SS, and Alloy 800). Because of their unique metallurgical characteristics, each alloy requires a specific pack chemistry to obtain the optimum coating composition. The ideal coating contains sufficient concentrations of the two elements for safe steady-state oxidation/corrosion resistance, without excessive contents which could lead to brittleness, unwanted phase changes and oxidant penetration in service.

The three coating elements Cr, Al, and Si are all ferrite stabilizers for steels. Therefore, ferritic stainless steels such as 409 SS remain ferritic at the coating temperature when Cr+Al or Cr+Si coating elements are diffused into the ferritic alloy. Plain- carbon and low-alloy steels are austenitic at the coating temperature (1000-1050°C) and the incorporation of Cr+Al or Cr+Si may result in the transformation of the austenite to a single-phase ferrite layer at the surface. This ferrite coating layer grows with time upon the transformation of the austenite core to a ferrite case, as dictated by the concentration gradients and the high diffusion coefficients in the ferrite.

High-alloy austenitic alloys can incorporate only limited concentrations of the coating elements into solid solution, and higher concentrations lead to a two-phase microstructure at the surface. Upon adding Cr+Al to austenitic alloys such as 304 and 316 SS, the inward diffusion of Al results in the precipitation of the compound NiAl within a ferrite matrix at the surface[5,8]. The resulting two-phase diffusion zone is tough mechanically and forms an alumina scale at steady state. Ni-base superalloys, when coated with Cr+Al, form an outward grown, beta-NiAl plus alpha-Cr layer, with a multiphase layer containing beta-NiAl, gamma-Ni_3Al, and carbides present underneath. In coating with Cr+Si, the Ni-silicides are generally avoided due to their low melting eutectics, brittleness and excessive spalling behavior upon oxidation[9].

Thus for each alloy coated, depending on its metallurgical factors and its intended service use, a unique pack cementation process must be developed to produce a corrosion-resistant coating with reasonable fracture toughness and excellent adhesion to the substrate. Such Al_2O_3- or SiO_2- forming "conversion" coatings are well bonded to the substrate by epitaxial interphase interfaces, and the coatings are inherently graded in composition so that sharp differences in physical properties such as coefficient of thermal expansion (CTE) are minimized.

The intention of this paper is to demonstrate the possibility to codeposit two or more elements into alloy substrates despite an inherent thermodynamic difficulty. Following a brief examination of the process thermodynamics and kinetics, examples for the codeposition of Cr+Al and Cr+Si into various steel substrates are presented in the form of metallography and concentration profiles. The very slow oxidation kinetics for these coatings correspond to those expected for steady-state alumina and silica scales. Pack cementation coatings for the more exotic materials nickel-base superalloys, niobium and Fe_3Al are also described.

THERMODYNAMICS AND KINETICS

In a cementation pack at the process temperature, the masteralloy and the halide salt activator react to form volatile metal halide species of significant partial pressures according to[10]

$$\underline{Me}(\text{alloy}) + AX_x(\text{s or l}) = MeX_x(\text{v}) + A(\text{l or v}) \qquad [1]$$

where $\underline{Me}$ is Cr, Al, or Si, A is Na, NH_4, etc., and X is F, Cl, or Br. In fact, multiple vapor species are formed for each element, e.g., Al, AlX, AlX_2, AlX_3, and Cr, CrX_2, CrX_3, and Si, SiX_2, SiX_3, and SiX_4. A partial pressure gradient for each vapor species, which supports vapor transport to the substrate surface, results from the high thermodynamic activity in the powder mixture and the lower activity at the substrate surface. At the surface, deposition of the desired coating element(s) occurs via the dissociation or disproportionation of the halide molecules, or by a displacement reaction with the substrate[10]. Finally, the coating elements interdiffuse with the metallic substrate producing some specific surface composition and microstructure, or perhaps another phase (compound).

The thermodynamics and kinetics of pack cementation have been studied rather extensively[10-18]. Earlier work by Levine and Caves[10] and Seigle et al.[11-13] concentrated on the aluminization of nickel and nickel-base alloys and Nciri and Vandenbulke[15] on iron-base alloy substrates. Levine and Caves[10] showed that the driving force for gaseous diffusion through the porous powder mixture is the negative gradient in partial pressure of the individual halide vapor species. The kinetics of vapor diffusion through a pack depleted at the surface were modeled using a Fick's first law expression. These calculations rationalize whether a particular halide vapor species will diffuse to the substrate. But solid-state diffusion is usually dominant in the rate-controlling step for the kinetics of the process. Overall in a single-component pack, an activity gradient from the pack to the substrate insures both the vapor phase and solid-state diffusion necessary to produce the diffusion coating.

Single elements are commonly deposited into metallic substrates by the pack cementation method, but a single-step process which would simultaneously codeposit multiple elements (e.g. Cr-Al or Cr-Si) into metallic substrates would be more effective because the resulting coatings would exhibit superior oxidation/corrosion resistance. According to the discussion above, one might suppose that a mixture of several pure elemental powders should produce simultaneous deposition. But this prospect fails in practice. Comparable negative pressure gradients for two (or more) elements, as required for dual gaseous diffusion, essentially never occurs because of large differences in the standard Gibbs energies of formation for their respective halide species (Fig. 1)[17,19,20]. However, binary Cr-rich alloys (Cr-Al and Cr-Si alloys) exhibit highly negative deviations from ideal thermodynamic behavior, so that such masteralloys can be used to reduce the activities of the Al or Si components by several orders of magnitude (Figs. 2a and 2b)[6,21]. Then by using such binary alloy powders, codeposition of Al and Cr into nickel- or iron-base alloys, or Cr and Si into iron-base alloys, can be achieved if an appropriately stable halide salt is also provided[4-7,22]. As shown in Fig. 3, the dilute Cr-Al or Cr-Si masteralloy powder, with reduced thermodynamic activities for Al or Si, respectively, generates lower vapor pressures for these otherwise favored halide species (i.e. AlX_x or SiX_y)[5-7,17,18]. In this way, the fluxes for the components to be codeposited are brought to comparable magnitudes so that simultaneous deposition results in the desired surface composition.

In addition, a third (or fourth) minor element might also be incorporated into the coating[7]. Two methods have been used to produce this further doping. A small amount of an oxide source of the desired element can be added to the pack mixture, replacing some of the inert filler. In this case, the dopant oxide must be reduced in the high halide activity of the pack, producing additional metal halide species according to

$$xMO_y(s) + yMeX_x(v) = xMX_y(v) + yMeO_x(s) \qquad [2]$$

where M is Zr, Y, or Hf and Me is Al or Si. Calculations of pack equilibria using ITSOL[23] and experiments using an atmospheric pressure sampling mass spectrometer have substantiated these reduction reactions for ZrO_2 and Y_2O_3 additions to Al_2O_3[24]. By a second method, the additional element could be introduced as the halide activator source (e.g. $ZrCl_4$, YCl_3, or $HfCl_4$). For example, $ZrCl_4$ can react with a Cr-Al masteralloy to produce both Al and Cr halides as well as significant partial pressures of the Zr halides[7]. If the substrate does not contain the third element, the necessary driving force exists for some codeposition.

CHROMIZING-ALUMINIZING

Low Alloy Steels

Low alloy steels (e.g. Fe-2.25Cr-1.0Mo-0.15wt%C) are commonly used in utility boilers, petrochemical plants, and coal gasification systems because of their excellent creep strength in service. These materials are exposed to a variety of corrosive environments, thereby requiring surface modification to improve the corrosion resistance of the substrate. A single-step, pack cementation process has been developed to produce the Kanthal composition (Fe-20Cr-4.5wt%Al) on the surface of Fe-2.25Cr-1.0Mo-0.15C alloys. Figure 4 shows a micrograph and concentration profile of the alloy coated in a pack containing 8 wt% of a 90Cr-10wt%Al masteralloy, NH_4Cl activator and Al_2O_3 filler heated at 1150°C for 6 h. A ferrite layer is formed initially on the substrate surface allowing for subsequent diffusion of Cr and Al into the ferrite matrix. Because ferrite has a very low carbon solubility, the rejection of carbon into the austenite phase at the ferrite/austenite interface prevents the formation of a $M_{23}C_6$ carbide at the surface. The resulting Cr/Al-enriched surface provides excellent steady-state oxidation resistance by an Al_2O_3 scale, even at temperatures as low as 700°C.

Stainless Steels

Chromized-aluminized coatings were achieved on several austenitic steels (e.g. 304, 316, and Alloy 800)[5]. Sufficient amounts of chromium and aluminum to produce alumina-forming coatings were incorporated into each alloy. The coating morphologies consisted of particles of beta-NiAl in a ferrite matrix, thus producing a mechanically tough microstructure. Compared to the initial work by Bangaru and Krutenat[8], the use of a Cr-Al masteralloy reduces the tendency for formation of an outward grown external NiAl layer which is brittle and entraps pack particles.

Nickel-Base Superalloys

Nickel-base superalloy turbine blades are commonly aluminized in a cementation pack for oxidation resistance. Unfortunately, aluminide coatings lack adequate resistance to hot corrosion caused by deposits of fused alkali sulfates. A chromium-modified aluminide coating would promise substantial improvements in the hot corrosion resistance of the coating[25]. In addition, a small amount of a reactive element (Zr or Y) is known to improve the adherence of protective alumina scales[26,27].

Two pack arrangements were used in the laboratory to produce Cr-enriched, aluminide coatings on several superalloys. By the simpler "powder contact" arrangement, the substrate is buried in direct physical contact with the powder mixture. By this method, some inert filler (Al_2O_3) and masteralloy particles are entrapped within the outer layer of the coated substrate. Such entrapped pack powder can act as an initiation site for thermal fatigue cracks or for local hot corrosion attack[7]. Such pack entrapment, however, can be eliminated by an "above pack" arrangement, whereby the test coupon is held isolated from contact with the pack by porous alumina cloth.

Figure 5 shows the microstructure of an Al_2O_3-free, Cr-alloyed beta-NiAl coating, with Zr dopant also deposited from the gas phase[7]. In this outward-grown beta-NiAl coating, a dispersion of alpha-Cr particles are precipitated near the original substrate surface and also grow inward from the gas phase at the coating surface. An interdiffusion zone between the outer layer and the original $\gamma+\gamma'$ substrate is comprised of ß-NiAl and γ'-Ni_3Al, $M_{23}C_6$, MC-type carbides, and sigma-phase[29]. The average bulk surface compositions for coated René 80 substrates resulting from the "above pack" arrangement are listed in Table I. These treatments were used to dope the coating with yttrium from either a Y_2O_3 or else YCl_3 source. For sufficiently high YCl_3 or Y_2O_3 contents, about 0.05 at% yttrium was deposited into the ß-NiAl coating layer according to electron probe microanalysis (EPMA) and x-ray fluorescence spectroscopy (XFS). Likewise, small zirconium contents were introduced by analogous processing.

Both hot corrosion and cyclic oxidation tests were performed on these RE doped, Cr-modified aluminide coatings. Figure 6 plots the weight changes for isothermal hot corrosion tests conducted for various exposure times using a 5 mg/cm^2 film of Na_2SO_4 applied prior to each exposure period. A commercial low activity aluminide coating, GE Codep, and the lower-Cr, $ZrCl_4$-activated coatings did not adequately protect the nickel-base superalloy during hot corrosion simulation, but the higher-Cr aluminide coatings provided a substantial improvement in coating lifetime[7,25].

Figure 7 is a plot of the weight changes for cyclic oxidation tests at 1100°C of coatings prepared by the "above pack" arrangements. Two of the Cr/RE-modified coatings produced acceptable protective scales of alpha-Al_2O_3

and $NiAl_2O_4$ spinel for 500 h. cycles. Coating failures occurred for RE-free and RE-lean coatings. As an important conclusion of this work, while every attempt to introduce both Cr and the RE into NiAl was not successful, indeed certain conditions were identified which achieved the goal.

Intermetallic Compound, Fe_3Al

Intermetallic compounds (e.g. Fe_3Al) have been candidate structural materials for various fossil fuel applications. Pure iron aluminides (Fe_3Al) have poor room temperature properties resulting from hydrogen embrittlement. But additions of chromium have been shown to improve its room temperature ductility. However, the resistance to high temperature sulfidation drops considerably because the formation of a protective alumina scale is impeded by Fe,Cr,Al sulfides[29]. A single-step, pack aluminizing treatment (Fe-42wt%Al masteralloy, NaF activator, 1200K) has been developed to produce a Cr-enriched, FeAl coating layer via an "above pack" method[30]. The resulting FeAl layer forms a protective alumina scale during oxidation exposure and provides excellent oxidation/sulfidation resistance to the Cr-alloyed Fe_3Al substrate.

However, the FeAl layer is also a brittle phase. Trace additions of boron are known to segregate to grain boundaries and thereby improve the room-temperature fracture toughness of bulk FeAl[31]. An FeAl coating layer with small additions of boron (1-3 at%) was produced by codeposition of Al and B in a pack containing 0.5-1 wt% FeB[30]. The boron addition reduced the microhardness of the FeAl layer from approximately 500 VHN to 350 VHN. As for bulk B-doped FeAl[32], the presence of B in the FeAl coating increased scale spallation during cyclic oxidation in air at 900°C. However, the weight losses were still below 2.5 mg/cm^2 after 1000 hrs[30].

Chromizing-Siliconizing

Ferritic Stainless Steel

Figure 8 shows the microstructure and concentration profiles for a chromized/siliconized coating on a ferritic 409 SS alloy. The thin dark horizontal line in the micrograph is the original coupon surface, showing some minor contribution by outward diffusion to coating growth. No substrate/coating interface is introduced in the absence of any phase change during the coating process and the dominant inward diffusion excludes both porosity and pack entrapment. The surface composition is Fe-23wt%Cr-2.5Si. Although no corrosion testing has yet been performed for the coating, this composition should provide excellent resistance to corrosion in both high temperature gaseous environments and in aqueous environments.

Low Alloy Steels

Figure 9 shows the microstructure and concentration profile for a chromized/siliconized Fe-0.5wt%Cr-0.5Mo-0.1C steel. Similar results were obtained for an AISI 1018 steel and an Fe-2.25wt%Cr-1.0Mo-0.15C alloy[33]. Again, the surface composition is high in chromium (25wt%Cr) with approximately 3wt%Si. As shown in Fig. 10, this coating has been tested in cyclic oxidation in air at 700°C and has shown extremely slow oxidation kinetics with no detectable spalling of the oxide scale. The remarkably low weight-gain (less than 0.2 mg/cm^2 for over 4.4 months at 700°C) for the coated Fe-2.25wt%Cr-1.0Mo-0.15C alloy has also been found for a similarly coated AISI 1018 steel. The very slow kinetics results from a slow growing silica layer beneath a thin outer chromia scale. Also shown for comparison in Fig. 10 are the isothermal oxidation kinetics of an uncoated Fe-2.25wt%Cr-1.0Mo-0.15C alloy[34] and an Fe-25wt%Cr binary alloy[35]. This Cr-Si coating has also shown negligible corrosion in an aerated 3.5%NaCl aqueous solution at room temperature.

Austenitic Steels

As discussed above, austenitic alloys can be coated by either diffusing the coating elements into solid solution or by transforming the matrix into a ferrite plus austenite two-phase field. For example, about 3wt% Si was diffused into the surface of the austenitic Alloy 800 without a significant change in microstructure. In contrast, Fig. 11 shows the transformation at the surface for 304 SS upon chromizing/siliconizing to form ferrite plus austenite[36]. Figure 12 presents the oxidation kinetics for these two coated alloys compared to the uncoated alloys upon cyclic oxidation at 1035°C in air. The coated Alloy 800 does suffer some scale spallation upon temperature cycling (approximately 1% of the surface area), but this behavior is an important improvement over the uncoated alloy. The coated 304 SS exhibited excellent high temperature oxidation resistance with no evidence of spalling, whereas the uncoated alloy did not form an effective adherent protective scale.

A key element in the reduction of oxidation kinetics is the presence of ferrite, with its much higher diffusion coefficients, at the surface. The high diffusivities for ferrite promotes the early formation and retention of the thermodynamically more stable oxide scales, i.e. chromium oxide rather iron oxide at an early stage of oxidation, and silica rather than chromia at steady state.

Niobium-Base Alloys

Because of their high solidus temperatures and reasonable creep strengths, niobium alloys have been considered as candidate materials for gas turbine engine applications. Unfortunately, niobium and its alloys have inherently very poor oxidation resistance because the oxide (Nb_2O_5) formed is not compact or resistant to permeation by molecular oxygen; therefore, a protective coating is necessary[37]. A new, two-step coating process has been developed to provide oxidation resistance for high temperature (1100-1500°C) service[38]. First, a diffusion barrier of molybdenum or molybdenum/ tungsten alloy is applied to the niobium substrate using a conventional sputtering or CVD technique. Then the substrate is silicided to form a $MoSi_2$ or $(Mo,W)Si_2$ layer by a NaF-activated, pack cementation method. Molybdenum disilicide has excellent high temperature oxidation resistance, providing a thin protective SiO_2 oxygen barrier.

Because of the large mismatch in CTE between $MoSi_2$ and SiO_2, the siliciding treatment has been modified to codeposit Si and Ge and thereby produce a $Mo(Si,Ge)_2$ or $(Mo,W)(Si,Ge)_2$ diffusion layer. Because the stabilities for the volatile fluorides of Si and Ge are reasonably similar, codeposition of Si and about 3 to 8 at% Ge to form $(Mo,W)(Si,Ge)_2$ has been achieved using mixtures of pure Si and Ge powders with a NaF activator at 1150°C for 16 h. Small germania additions to silica greatly increase its CTE, and thereby decrease the CTE mismatch between the scale and the substrate, which improves the cyclic oxidation behavior of the coating[39].

In a recent study, six out of eight $(Mo,W)(Si,Ge)_2$-coated pure niobium coupons survived cyclic oxidation in air for 200, one-h. periods at 1370°C with weight-gains of only 1.2-1.6 mg/cm^2. Premature failures occurred on two coupons due to excessive growth of Nb_2O_5 initiated at cracks in the coating, but the Nb_2O_5 formation was not catastrophic. One of the cyclic oxidation tests of a $(Mo,W)(Si,Ge)_2$-coated coupons was extended to 500 h. cycles without failure[40]. These results indicate that this multicomponent silicide coating offers significant promise to protect niobium-base alloys in oxidizing environments at very high temperatures.

CONCLUSIONS

Ternary alloys promise improved resistance to high temperature oxidation and hot corrosion. Despite an inherent thermodynamic problem, codeposition of two or more elements into diffusion coatings can be achieved by the halide-activated pack cementation method. Effective multicomponent coatings have been demonstrated for a wide variety of metallic substrates.

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Figure Captions

Figure 1: Log pressure of gaseous halides as a function of temperature in NaCl-activated packs containing pure Al, Cr, and Si.

Figure 2: Activity data as a function of solute content for (a) Al and Cr in a Cr-Al alloy at 1073, 1173, and 1273 K[21] and (b) Si and Cr in a Cr-Si alloy at 1323 K[6].

Figure 3: Equilibrium partial pressures of metallic halides in (a) NH_4Cl-activated packs containing Cr-Al masteralloys and Al_2O_3 filler at 1150°C and (b) NaCl-activated packs containing Cr-Si masteralloys and SiO_2 filler at 1050°C.

Figure 4: Microstructure and concentration profiles of coated Fe-2.25Cr-1.0Mo-0.15C steel using "lean" pack of 90Cr-10wt%Al masteralloy (8wt% of pack) and NH_4Cl activator diffused at 1150°C for 6 hours.

Figure 5: Cross-sectional micrograph of a René 80 alloy substrate treated at 1150°C for 24 hours in a 2wt% ZrO_2 and NH_4Cl-activated pack ("above pack") with 25 wt% of a 90Cr-10wt%Al masteralloy.

Figure 6: Isothermal hot corrosion of René 80 alloy substrate coated by a "powder contacting" method in 0.1% SO_2/O_2 at 900°C with periodic Na_2SO_4 recoating.

Figure 7: Specific weight changes for 1100°C cyclic oxidation in air of coated René 80 alloy substrates versus cycle time for the "above pack" arrangements.

Figure 8: Microstructure of coating and concentration profiles for 409 SS using 90Cr-10wt%Si masteralloy and NaF activator diffused at 1050°C for 16 hours (SiO_2 filler).

Figure 9: Microstructure of coating and concentration profiles for Fe-0.5Cr-0.5Mo-0.1wt%C steel using 90Cr-10wt%Si masteralloy and NaF activator diffused at 1050°C for 16 hours (SiO_2 filler).

Figure 10: Plot of weight-gain versus time for the cyclic oxidation in air at 700°C of coated samples with surface compositions of 34Cr-3Si. Each indicated point represents the weight-gain measured after cooling from 700°C to room temperature.

Figure 11: Microstructure of coated 304 SS using 90Cr-10wt%Si masteralloy and NaF activator diffused at 1150°C for 16 hours (Al_2O_3 filler).

Figure 12: Plot of weight-gain versus time for the cyclic oxidation in air at 1035°C of coated and uncoated 304 SS and Alloy 800. Each indicated point represents the weight-gain measured after cooling from 1035°C to room temperature.

Table I: Surface analysis results (EPMA) of René 80 substrates coated for 24 hours at 1150 °C in Ar gas.

"Above Pack"

			Average Bulk Surface Composition (a/o)				
Activator	Masteralloy	(wt.)	Ni	Al	Cr	Zr	Y
NH_4Cl, ZrO_2 1	92.5Cr-7.5Al,	(25)	47.6	36.2	7.6	.18	-
$ZrCl_4$, 4w/o	" "	"	49.9	33.4	8.1	.22	-
NH_4Cl, Y_2O_3 2	" "	"	47.9	38.9	6.4	-	.02
YCl_3, Y_2O_3 3	" "	"	50.2	36.7	6.3	-	.01
" , $CrCl_2$ (1:1)	" "	"	47.7	37.2	7.6	-	.02
" , " (2:1)	" "	(20)	50.9	34.8	7.5	-	.00
$ZrCl_4$, 4 w/o	75Ni-25Al	(25)	44.5	40.9	1.9	.12	-

1=2 w/o ZrO_2

2=4 w/o Y_2O_3

3= " both YCl_3 and Y_2O_3

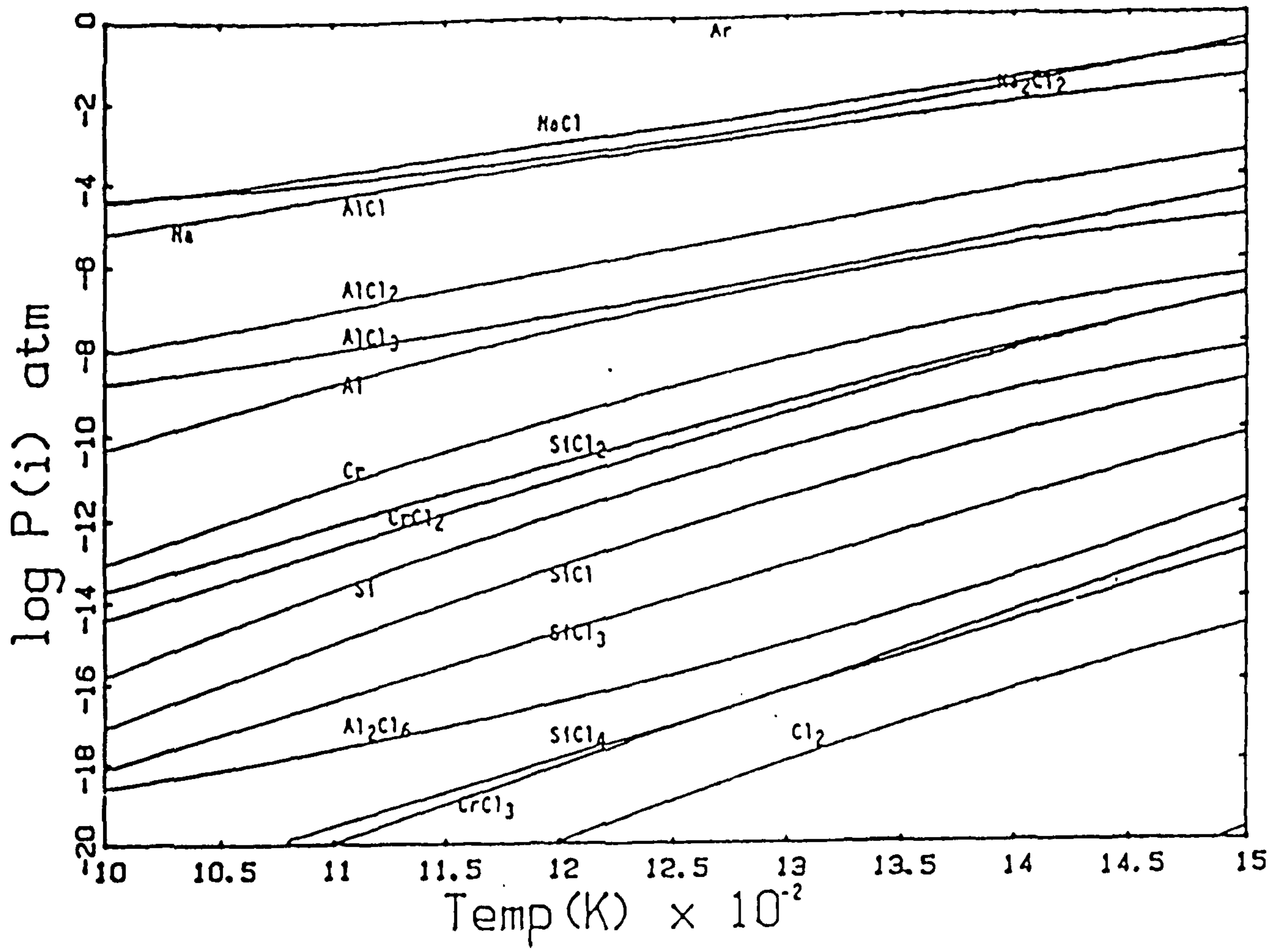


Figure 1: Log partial pressure of gaseous halides as a function of temperature in NaCl-activated packs containing pure Al, Cr, and Si.

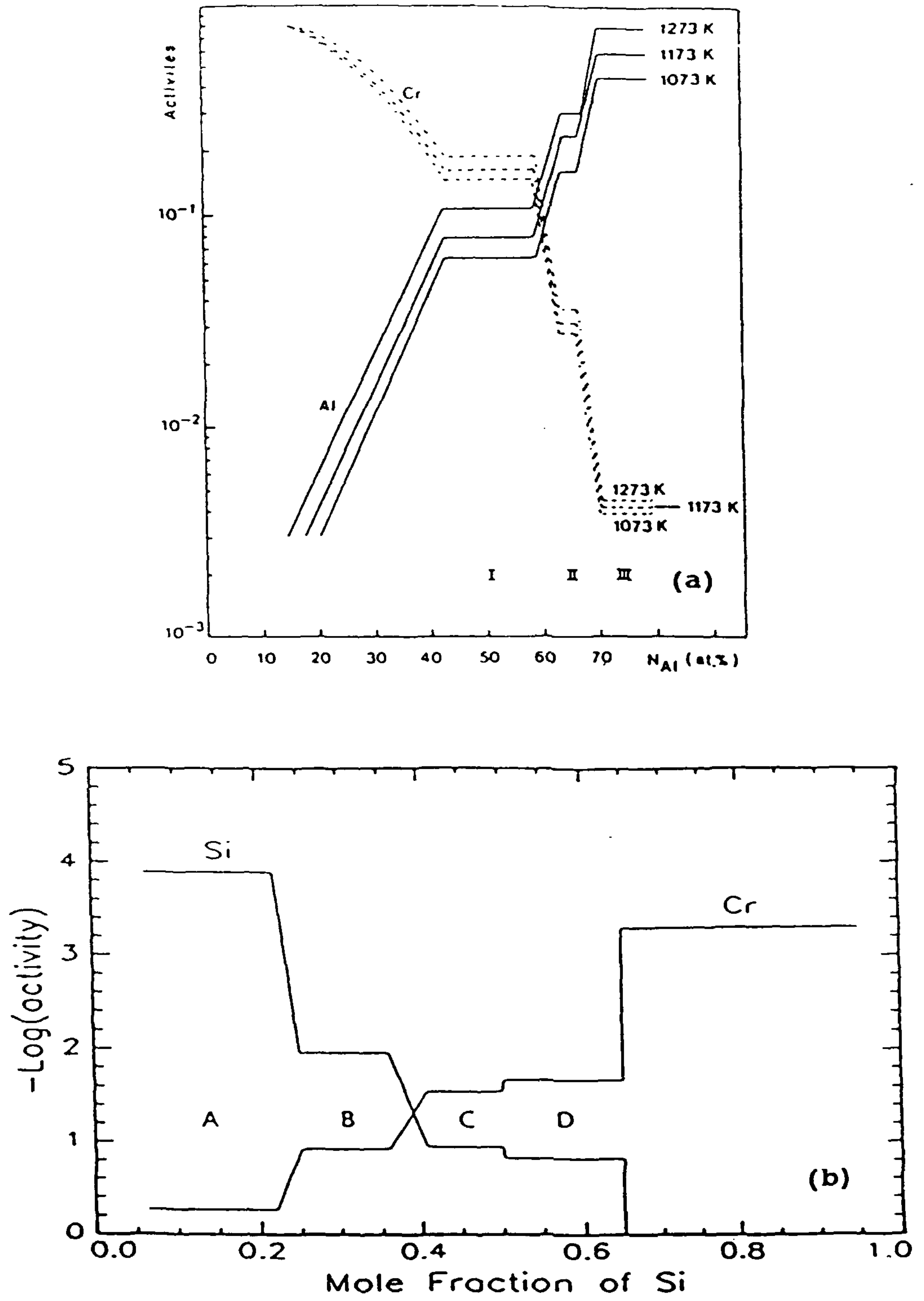


Figure 2: Activity data as a function of solute content for (a) Al and Cr in a Cr-Al alloy at 1073, 1173, and 1273 K[21] and (b) Si and Cr in a Cr-Si alloy at 1323 K.

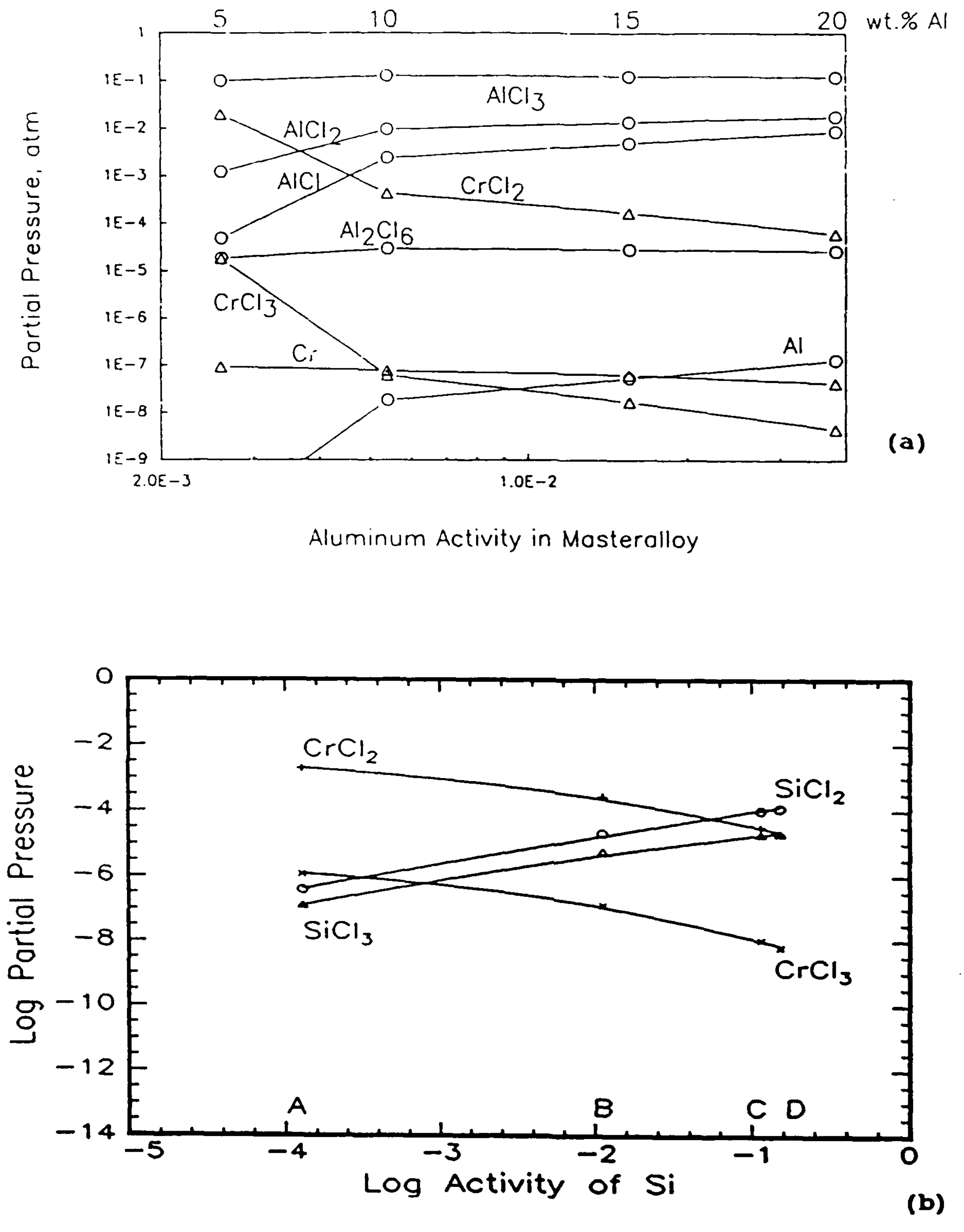
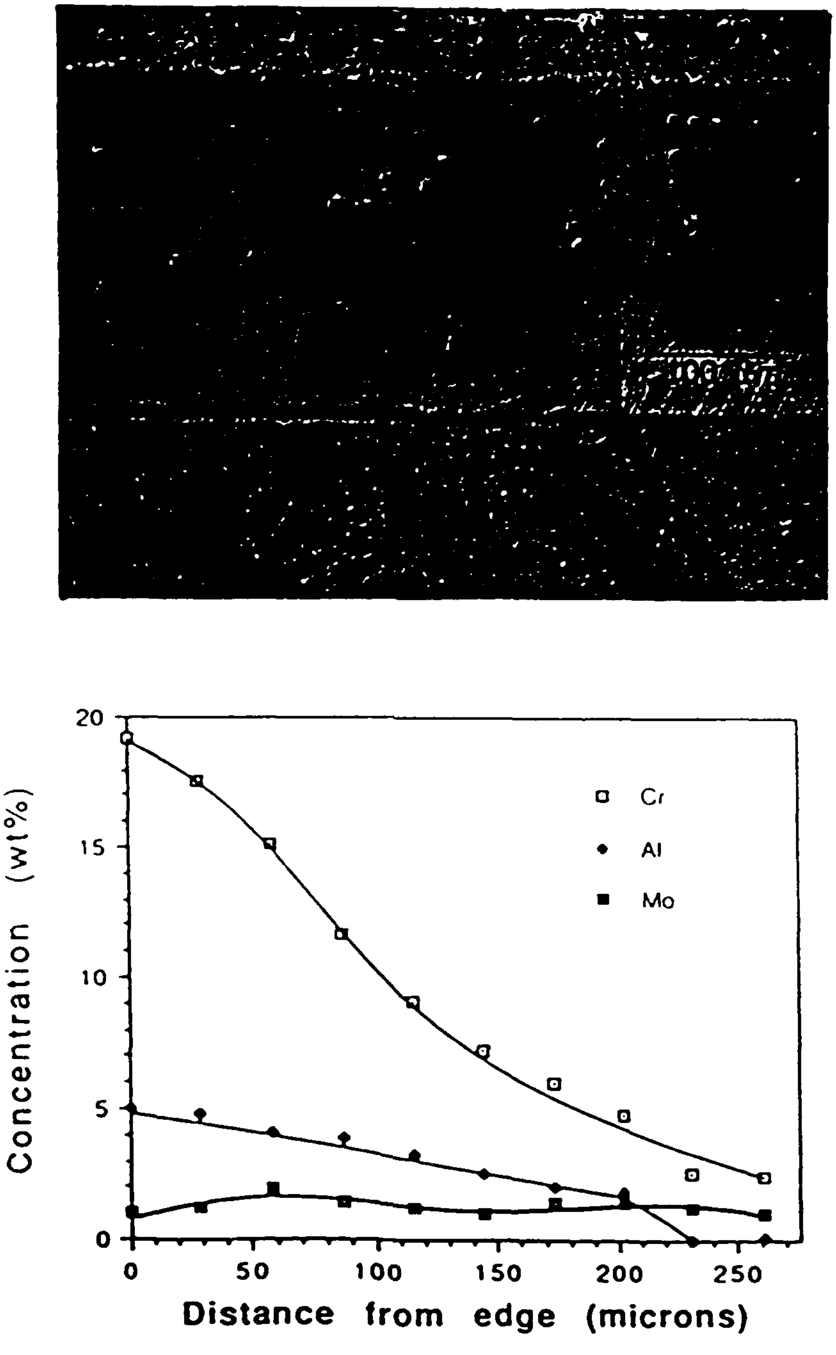


Figure 3: Equilibrium partial pressures of metallic halides in (a) NH_4Cl-activated packs containing Cr-Al masteralloys and Al_2O_3 filler at 1150°C and (b) NaCl-activated packs containing Cr-Si masteralloys and SiO_2 Filler at 1050°C.



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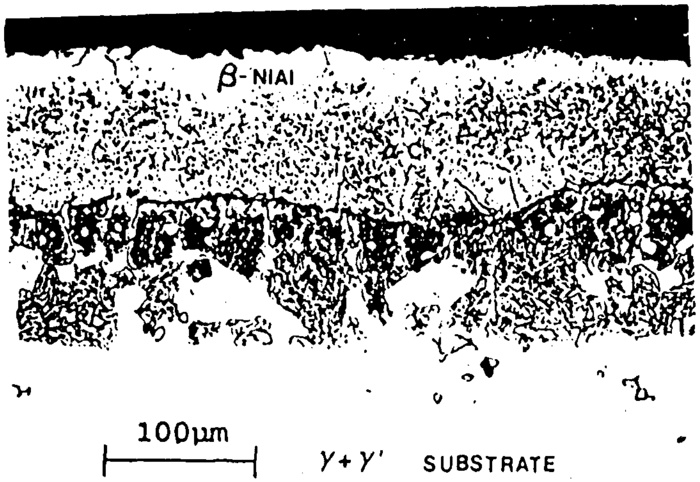

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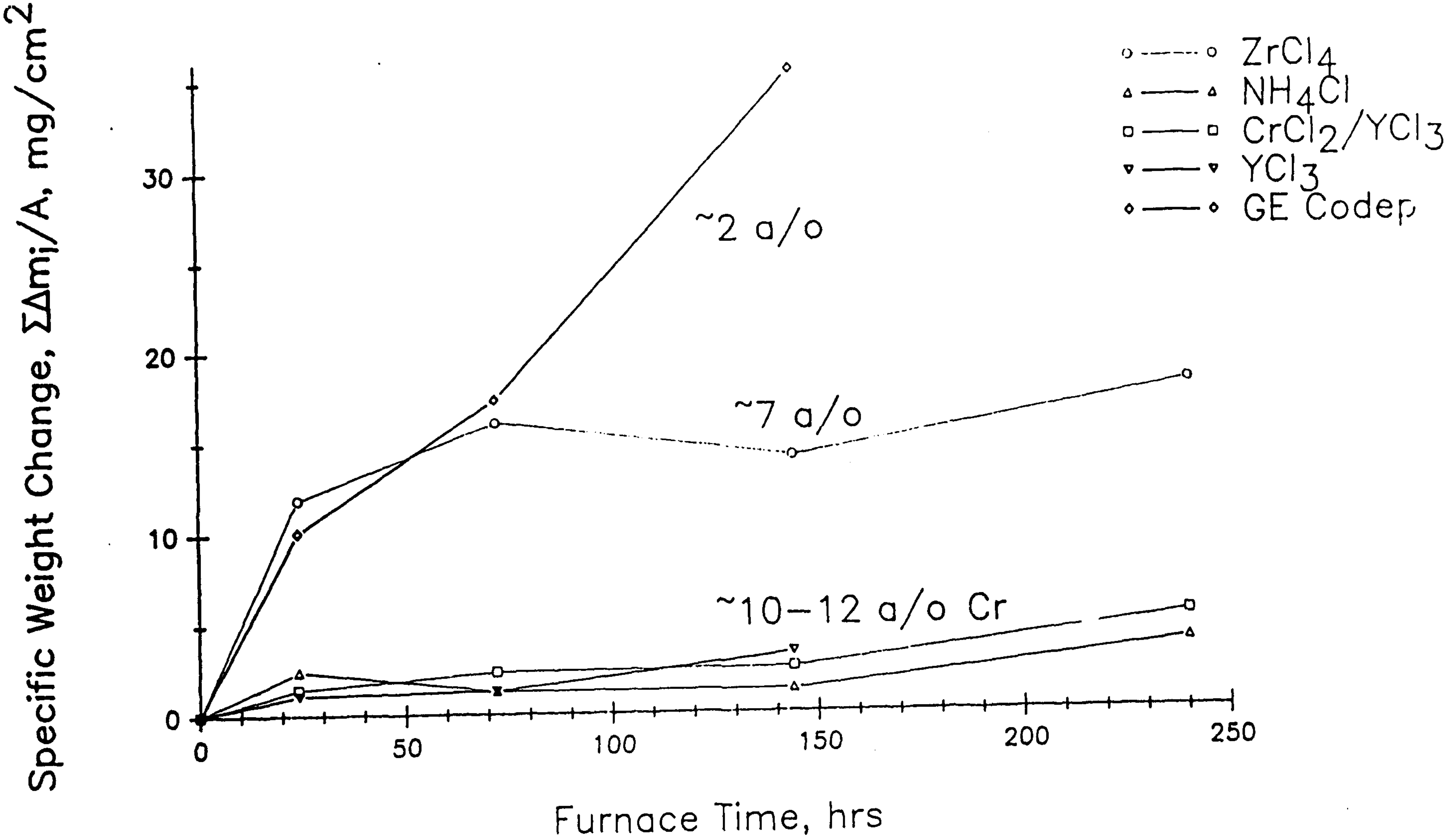

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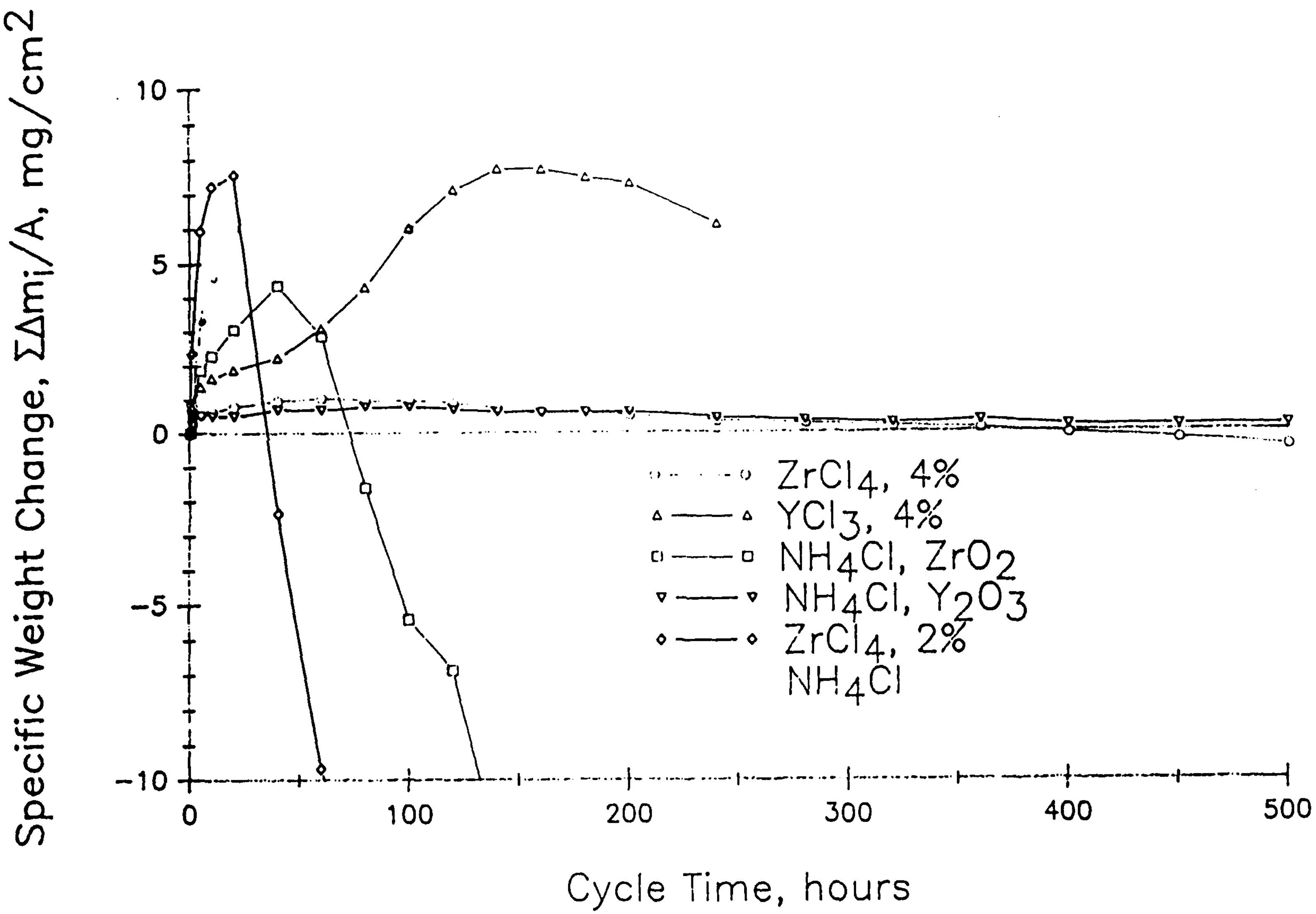
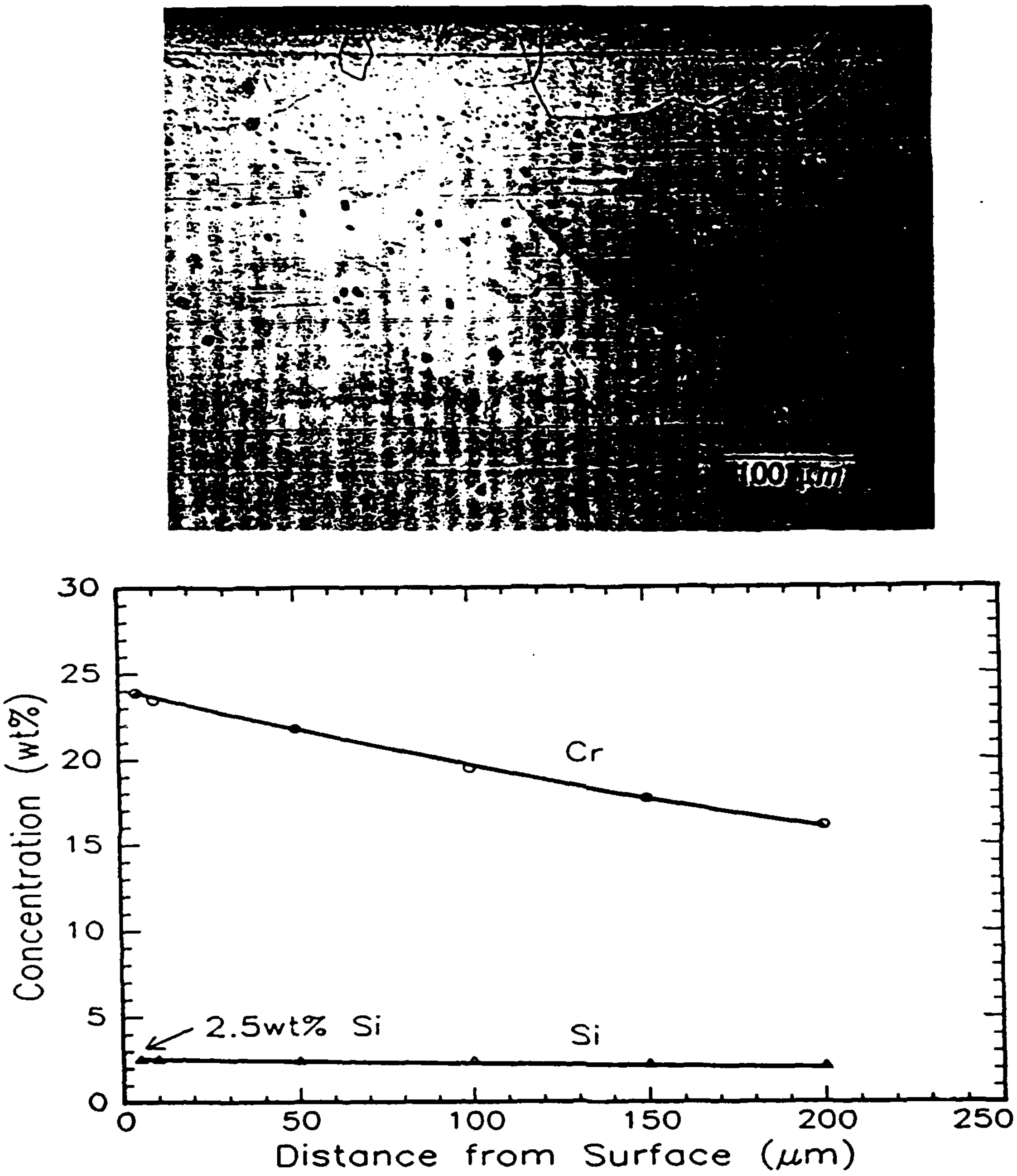


Figure 7: Specific weight changes for 1100°C cyclic oxidation in air of coated René 80 alloy substrates versus cycle time for the "above pack" arrangements.



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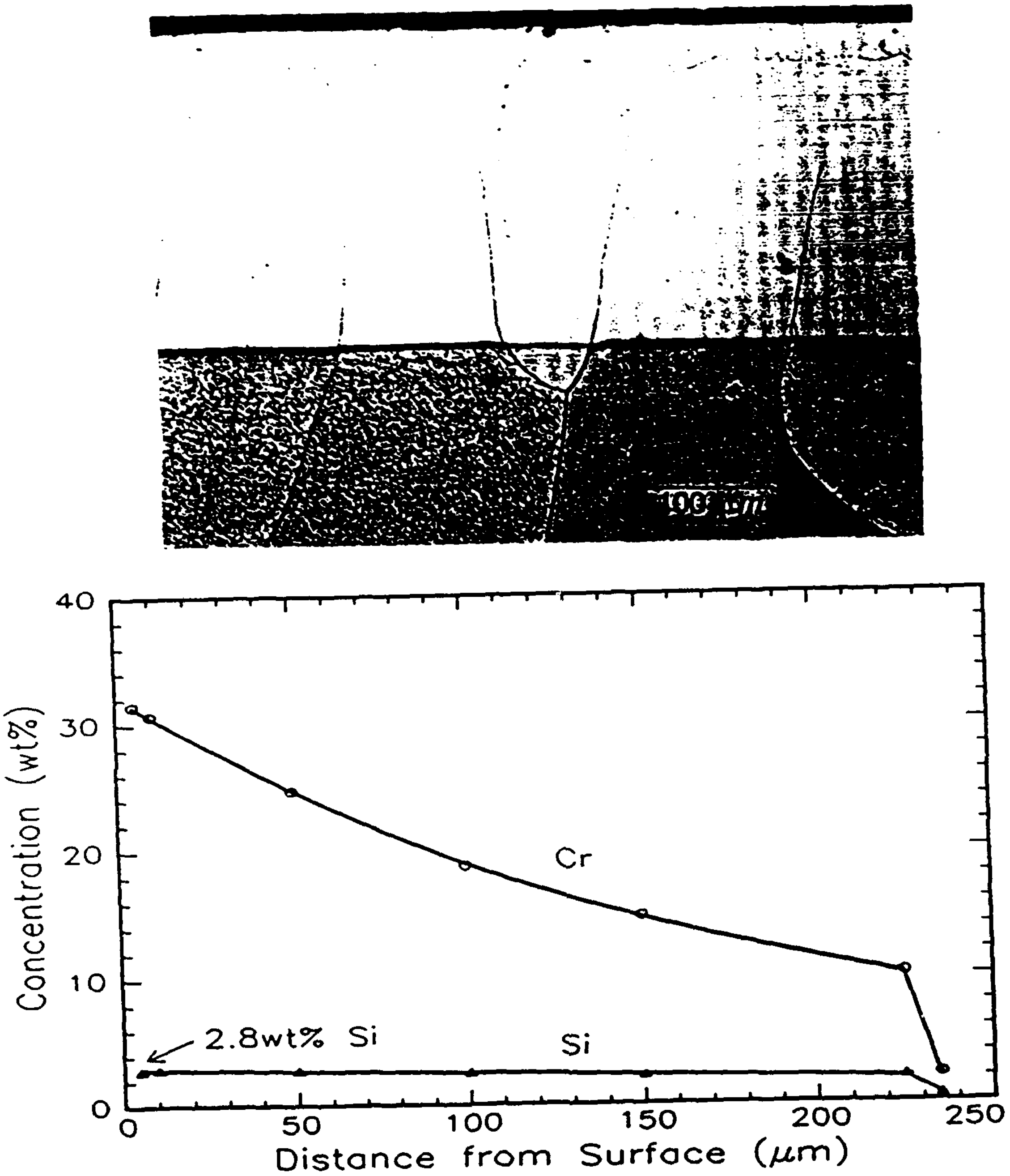
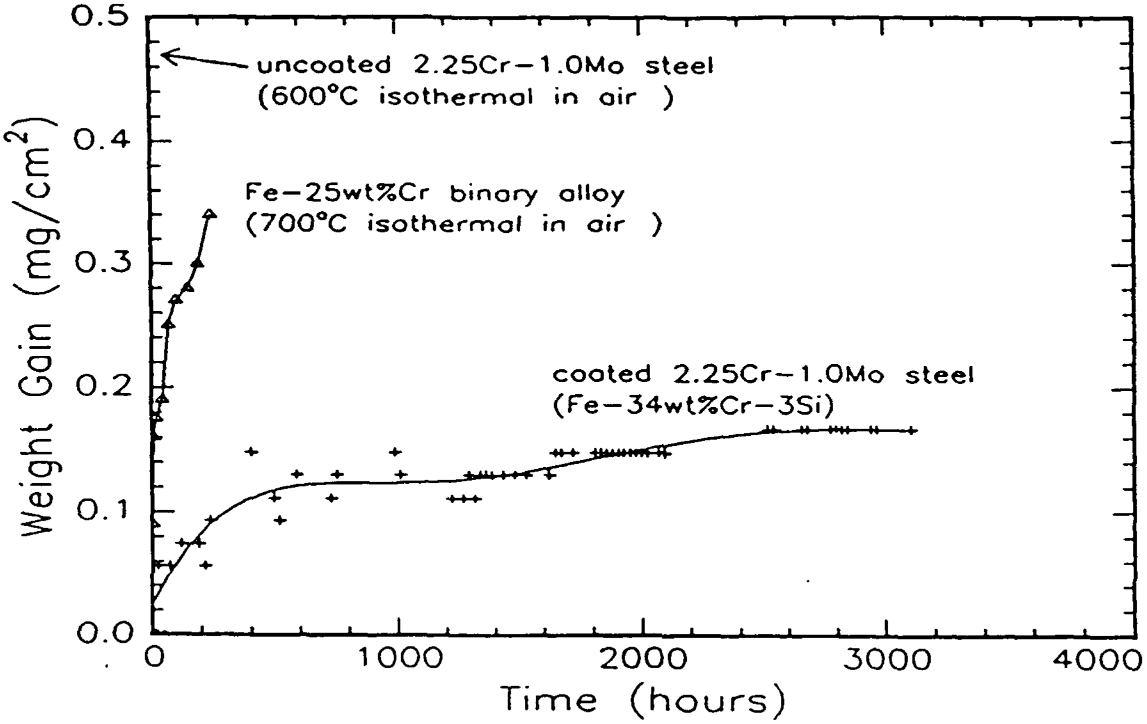


Figure 9: Microstructure of coating and concentration profiles for Fe-0.5Cr-0.5Mo-0.1wt%C steel using 90Cr-10wt%Si masteralloy and NaF activator diffused at 1050°C for 16 hours (SiO_2 Filler).



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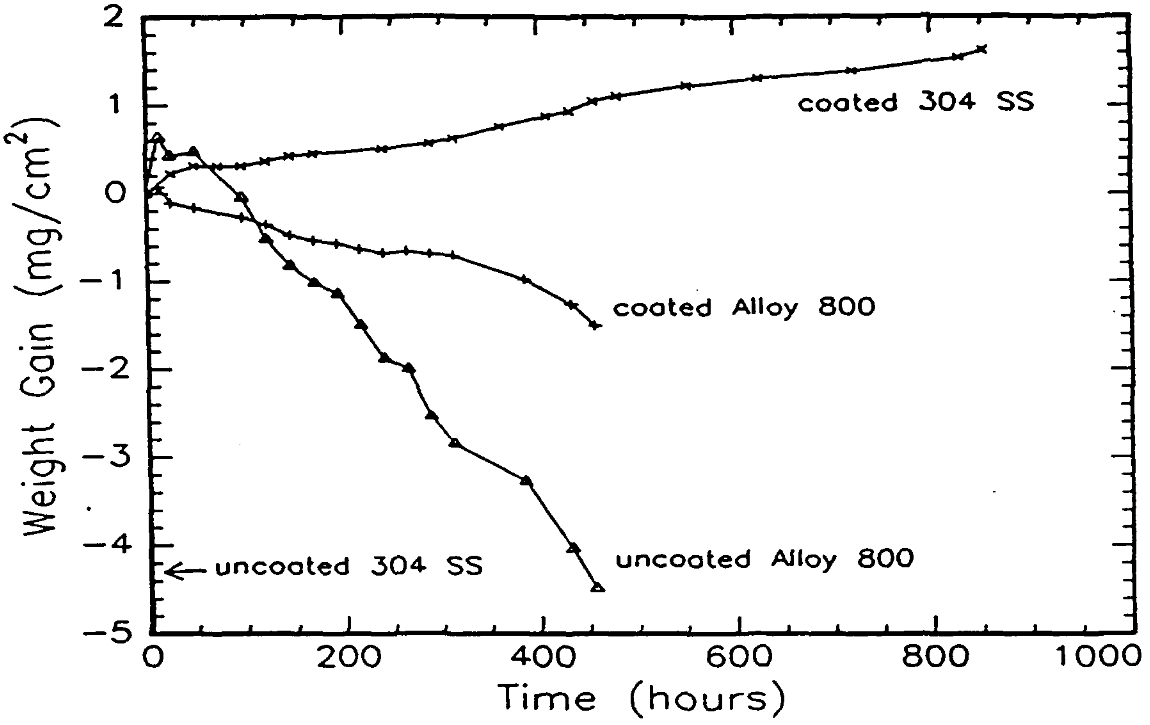

Figure 12: Plot of weight-gain versus time for the cyclic oxidation in air at 1035°C of coated and uncoated 304 SS and Alloy 800. Each indicated point represents the weight-gain measured after cooling from 1035°C to room temperature.