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THERMODYNAMICS OF SIMULTANEOUS CHROMIZING-ALUMINIZING
IN HALIDE-ACTIVATED CEMENTATION PACKS

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Thermodynamics of Simultaneous Chromizing-Aluminizing
in Halide-Activated Cementation Packs

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ABSTRACT

The equilibrium partial pressures of the gaseous species in halide activated cementation packs have been determined with the computer program SOLGASMIX. The effects of the activator and the composition of the masteralloy on the coating process have been investigated. The activities of Al and Cr have been incorporated into the calculations and the results indicate that codeposition of Al and Cr is possible using NaCl, AlCl₃, or NH₄Cl as activators and Al-Cr masteralloys with compositions between 90 w/o and 95 w/o Cr. In contrasting the coating of Ni or Fe substrates, the partial pressures of Ni halides are considerably lower than those of the Fe halides, indicating that displacement reactions occur when Fe substrates are coated. The upper limits for the surface composition of the coating have been predicted for different masteralloy compositions,

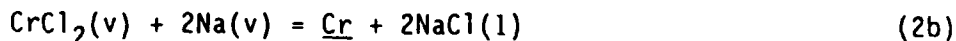
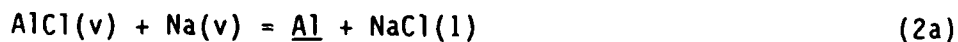
INTRODUCTION

Pack cementation is a modified chemical vapor deposition process carried out in a closed container at elevated temperatures (usually 1000°C). Aluminide, silicide and chromium coatings for hot corrosion and oxidation resistance are applied using this technique especially for aircraft turbine components.

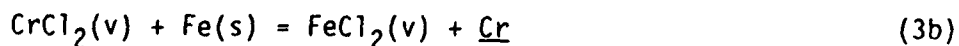
The pack cementation process is usually carried out at constant temperature and pressure. A pack typically consists of the substrate(s) to be coated and powders of an inert filler, a masteralloy rich in the element(s) to be deposited and an activator salt. The activator salt reacts with the masteralloy to generate volatile metallic halides which diffuse through the porous filler material (usually alumina) to the substrate surface [Fig. 1]. At the substrate surface, the metallic halide vapors participate in one or more of several possible reactions. Disproportionation reactions at the surface of the substrate:



Reactions of the coating element to deposit salt on the substrate:



Reactions with the environment or the substrate:



All of the reactions 1-3 result in the deposition and subsequent solid state diffusion of the desired coating element into the substrate.

The coating process is generally carried out in an inert or reducing atmosphere. Flowing argon is commonly used as an inert shroud while

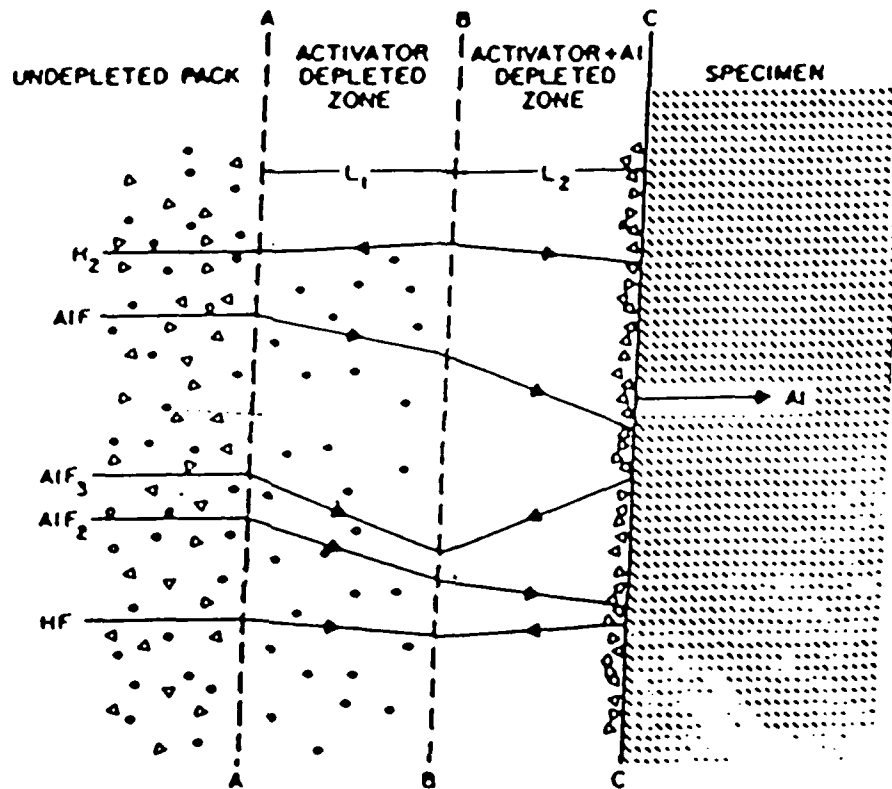


Figure 1: Schematic Diagram of Model Proposed by Levine and Caves [6] and Seigle [7] for Packs Coated with Pure Al as the Masteralloy.

hydrogen or hydrogen mixed with argon is used as a reducing atmosphere to aid in the coating kinetics as in reaction (3a).

The substrate may also play a role in the cementation process. If an iron or iron-base alloy is coated, the substrate can undergo a reaction of the type shown in (3b) because the partial pressures of the iron halides are significant. But if a Ni-substrate is used, then reactions of the substrate with the halide environment are not significant since the partial pressures of the nickel halides are comparatively small.

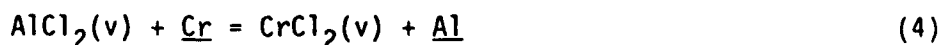
Current commercial practice almost always involves the deposition of single elements (Al, Cr, or Si) to form coatings. However, frequently combinations of two of these elements are advantageous to provide enhanced corrosion and oxidation resistance, e.g., Cr plus Al, or Cr plus Si. Currently, two-step coating procedures have been adopted to incorporate Cr and Al sequentially into the substrate [1,2]. A single step codeposition process would be cheaper, easier, and better than a two-step process, and the resulting concentration profiles would provide more effective oxidation/hot corrosion resistance. Restall [2] and Walsh [3] have stressed that simultaneous codeposition of Al and Cr is generally not possible because of the considerable difference in the stabilities of the volatile halides of Al and Cr. Recently, Rapp, Wang and Weisert [4] have developed procedures for the codeposition of Al and Cr simultaneously into iron-base alloys to achieve Kanthal-like surface compositions on pure Fe and Fe-2.25 Cr-1 Mo substrates. Because of the considerable controversy and difficulty associated with the codeposition process, an evaluation of the pack thermodynamics would assist in judging the feasibility of such a process.

THERMODYNAMICS

The thermodynamics of the coating process have been analyzed by several workers [3, 5-7]. However, all previous workers except Walsh [3] and Nciri and Vandenbulcke [5] have used unit activities for the coating components in their calculations. These workers determined the partial pressures of vapor species for packs with reduced, but still high, Al activities and an absence of Cr. In the following, equilibrium partial pressures for the Al and Cr halides are calculated for low Al activity packs containing Cr-Al masteralloys and the activators NaCl, NH_4Cl , AlCl_3 , CrCl_2 , NaF or AlF_3 . The codeposition of Al and Cr into Ni-base and Fe-base alloys is discussed.

Simultaneous Codeposition of Chromium and Aluminum

Marijnissen [8] has shown that by choosing a special pack composition, simultaneous deposition of Cr and Al into a Ni-base alloy (IN738) at 1100°C is possible. The chemical equilibrium in the pack used as the basis for codeposition of Cr and Al is given as:



By adjusting the aluminum activity in the pack, a_{Al} , the partial pressures of volatile Al halides can be moderated leading to codeposition [9]. However, the required composition of the source alloy and the effect of the activator on the coating process have not been treated.

Simultaneous chromizing-aluminizing is critically dependent on the choices of the masteralloy and the activator [4]. For unit Al activity the partial pressures of the aluminum halides are several orders of magnitude higher than those for the chromium halides at unit chromium activity. Then in order to achieve codeposition, the aluminum activity has to be lowered by a few orders of magnitude to generate comparable Al and Cr halide partial pressures. Johnson, Komarek and Miller [10] have determined the activities of Al and Cr in binary Al-Cr alloys at 1273K [Fig. 2]. The maximum solid solubility of Al in Cr is 43 at% Al; for all Al contents lower than this,

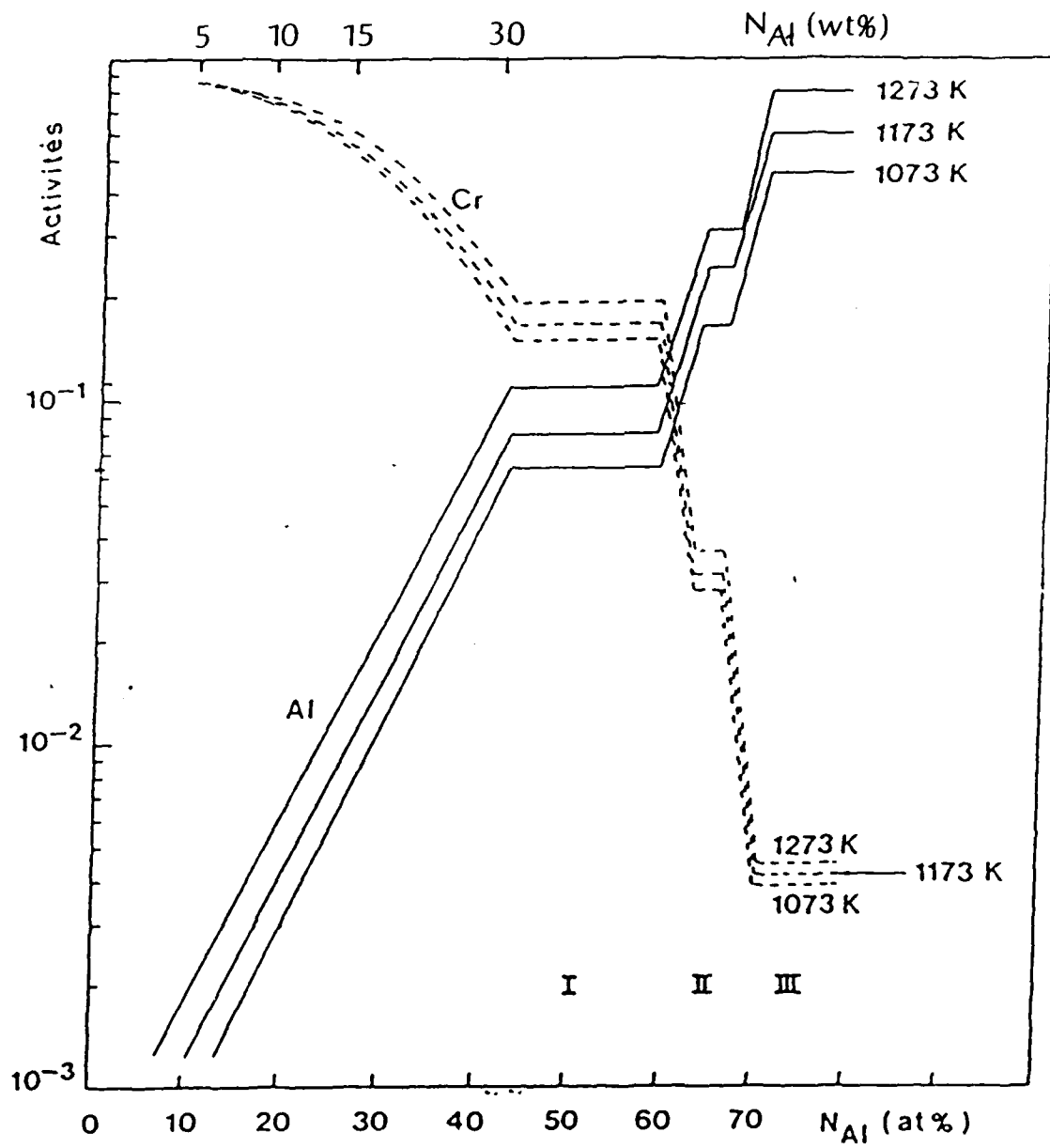


Figure 2: Activities of Al and Cr as a function of atom% Al in the Al-Cr system (Johnson, Komarek and Miller [10]).

Table I: Standard Gibbs energies of formation of sodium, aluminum, chromium and iron halides (1273 K)

Gas Phase	ΔG^0 (Kcal/mol)	Gas Phase	ΔG^0 (Kcal/mol)
AlCl	-36.275	AlF	-86.480
AlCl ₂	-75.930	AlF ₂	-173.050
AlCl ₃	-123.340	AlF ₃	-270.130
Al ₂ Cl ₆	-233.500	Al ₂ F ₆	-541.510
CrCl ₂	-48.010	CrF	-27.320
CrCl ₃	-88.590	CrF ₂	-115.610
CrCl ₄	-70.790	CrF ₃	-196.180
FeCl	25.920	FeF	-19.810
FeCl ₂	-47.140	FeF ₂	-103.180
FeCl ₃	-54.430	FeF ₃	-186.100
NaCl	-56.825	NaF	-83.580
Na ₂ Cl ₂	-126.490	Na ₂ F ₂	-182.300
Condensed Phases		Condensed Phases	
		AlF ₃	-281.850
CrCl ₂	-59.060	CrF ₂	-146.070
		CrF ₃	-212.081
FeCl ₂	-48.100	FeF ₂	-127.690
NaCl	-69.945	NaF	-103.960

Table II: Thermodynamic calculations of the equilibrium composition of a pack by SOLGASMIX under argon at 1273K; activator NaCl; $P_{\text{total}} = 1 \text{ atm}$; in the masteralloy, $a_{\text{Al}} = 0.004$ and $a_{\text{Cr}} = 0.83$ (90wt%Cr-10wt%Al)

<u>PHASE GAS</u>			
SPECIES	P/ATM	SPECIES	P/ATM
Ar	.99439E+00	Al ₂ O	.10845E-11
NaCl	.55918E-02	Al	.39899E-12
Na	.11230E-04	Al ₂ Cl ₆	.34681E-13
AlCl ₃	.24806E-05	Cl ₂	.76059E-14
CrCl ₂	.67966E-06	Al ₂ O ₂	.89159E-19
CrCl ₃	.54478E-06	AlO ₂	.21318E-25
AlCl	.37479E-06	CrO ₂	.16328E-25
AlCl ₂	.20964E-06	O ₂	.28967E-30
Cr	.11112E-08	CrO ₃	.25508E-37
Cl	.83487E-09		

<u>MASTERALLOY</u>	
SPECIES	EQ. MOLES
Cr	.19900E+00
Al	.42567E-01

<u>INVARIANT CONDENSED PHASES</u>	
SPECIES	EQ. MOLES
Al ₂ O ₃	.36767E+00
NaCl	.17000E-01
CrCl ₂	.00000E+00
Cr ₂ O ₃	.00000E+00

INITIAL INPUTS: $n_{\text{Al}} = .735$ mole; $n_{\text{O}} = 1.103$ moles $n_{\text{Na}} = .017$ mole; $n_{\text{Cl}} = .017$ mole
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the activity of Al is much lower than that of Cr. For the Cr-rich, Cr-Al alloys, the highly negative deviation from ideal solution behavior provides an Al activity of 0.001 at 9 at% Al. Therefore, the composition of a Cr-Al masteralloy can be manipulated to adjust the activities of Al and Cr so that comparable partial pressures of the halides of Cr and Al are generated in the pack for codeposition of Cr and Al. The specific activator also affects the magnitudes and ratios of the partial pressures.

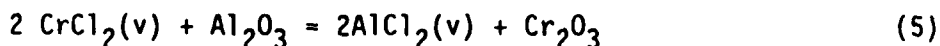
The calculation of the equilibrium partial pressures of the gaseous species for a given activator salt and given thermodynamic activities of the Cr and Al components in the condensed phase has been carried out with the computer program SOLGASMIX-PV developed by Ericksson [11] and modified for microcomputer use by Lin [12] and Morris et al [13]. The program is based on the conservation of mass and the minimization of the Gibbs energy of the system to arrive at the equilibrium gas composition.

The calculations were performed for 1273K in an Ar atmosphere. The input parameters for the program were fixed on the basis of 50 gms of pack containing 73 wt% Al₂O₃, 25% Cr-Al masteralloy and 2% activator salt. A static Ar gas was assumed. The input amount of Ar was calculated by treating it as an ideal gas and determining the number of moles contained in a retort of volume 40 cm³. The initial bulk compositions were used as the input for all computations [6]. In practice, where flowing Ar is used, some loss of the activator might result but no allowance has been made for this loss.

The activities of Al and Cr input into the program were taken from Johnson et al [10]. The free energy values for most species were provided by Pankratz [14] with the exception of gaseous Cr chlorides [15] and gaseous Cr fluorides [16,17]. Table I shows the standard Gibbs energies of formation for the halides of Na, Al, and Cr (gaseous and condensed) used in the computations.

RESULTS AND DISCUSSION

Table II shows the equilibrium partial pressures of the gaseous species and the number of moles of solid species in a NaCl-activated pack with a 90 Cr-10 w/o Al masteralloy. Because the chlorine activity for this pack is necessarily high, the partial pressures of AlCl₃ and CrCl₃ are also high. However, these species cannot be expected to deposit Al or Cr, since they could only function to return the halogen from the substrate to the pack. However, the dominant deposition species AlCl and CrCl₂ have comparable magnitudes in the pack, so codeposition of Cr and Al seems feasible. No change occurs in the number of moles of alumina at equilibrium, which confirms its role as an inert filler. The oxidation of Cr to Cr₂O₃ by the following reaction:



does not occur.

Figures 3 through 7 present the partial pressures of the gaseous species as a function of the activity of Al in NaCl-, NH₄Cl-, CrCl₂-, NaF- and AlF₃- activated packs on Ni and Fe substrates. Since the partial pressure of the gaseous halides of Ni are insignificant, Figures 3a through 7a represent the partial pressures of gases in the pack while Figures 3b through 7b represent the partial pressures at an Fe substrate-gas interface.

Figure 3a shows that the partial pressure of chromium dichloride is greater than that for aluminum monochloride in a NaCl-activated pack only at low Al activities; a crossover occurs at an Al activity corresponding to approximately 10 wt% Al. This crossover composition depends upon the choice of the activator which decides the chlorine activity for a given pack. For a given masteralloy, a less stable halide activator salt produces a higher halogen activity and raises the ratio of partial pressures for the chromium

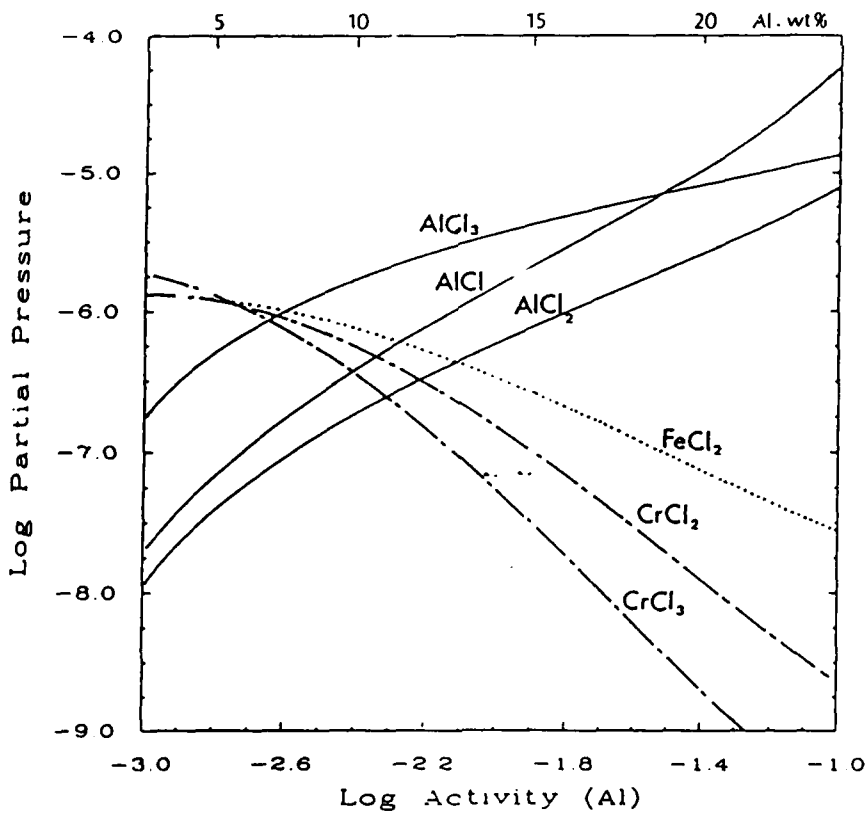
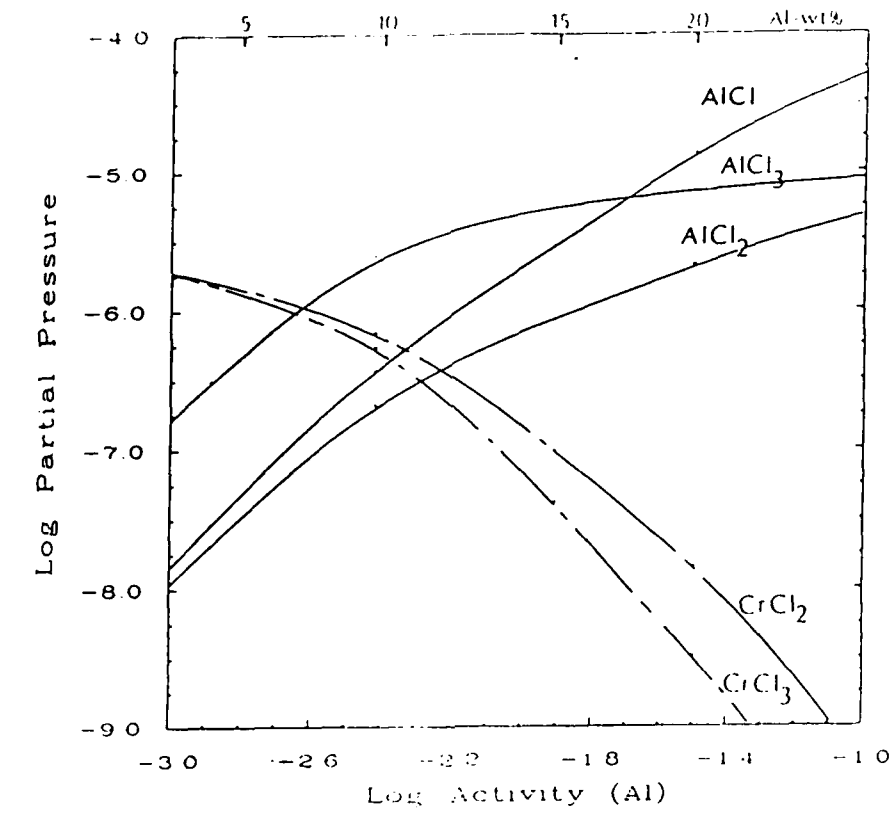


Figure 3: Equilibrium partial pressures of gaseous species in an NaCl-activated pack as a function of Al activity in the masteralloy (Ar, 1273 K) (a) in the pack (b) at an Fe-substrate.

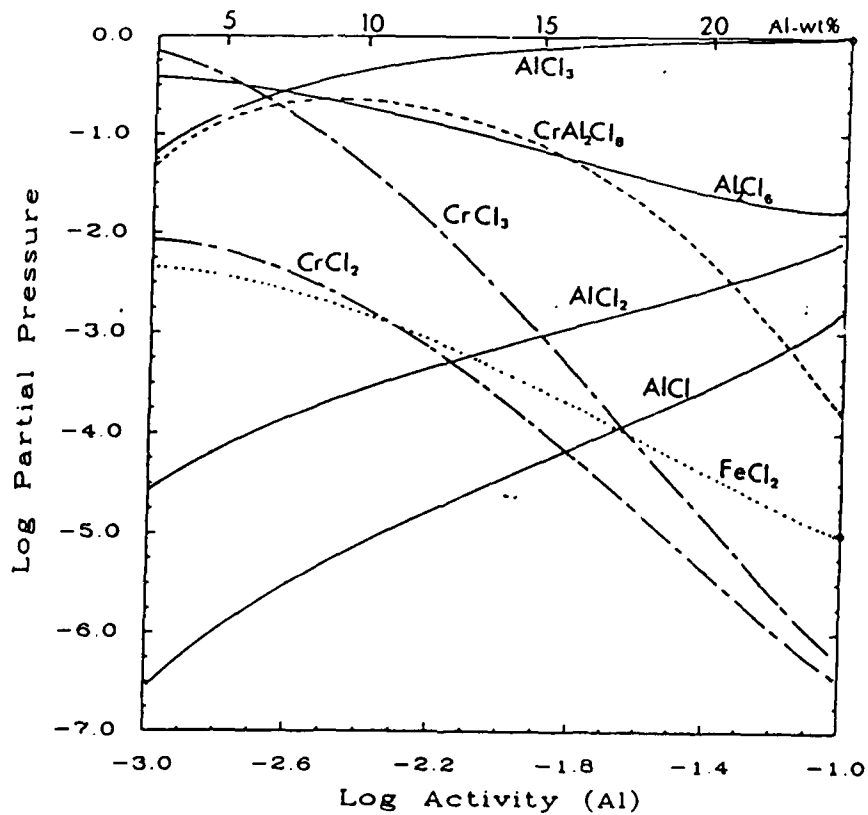
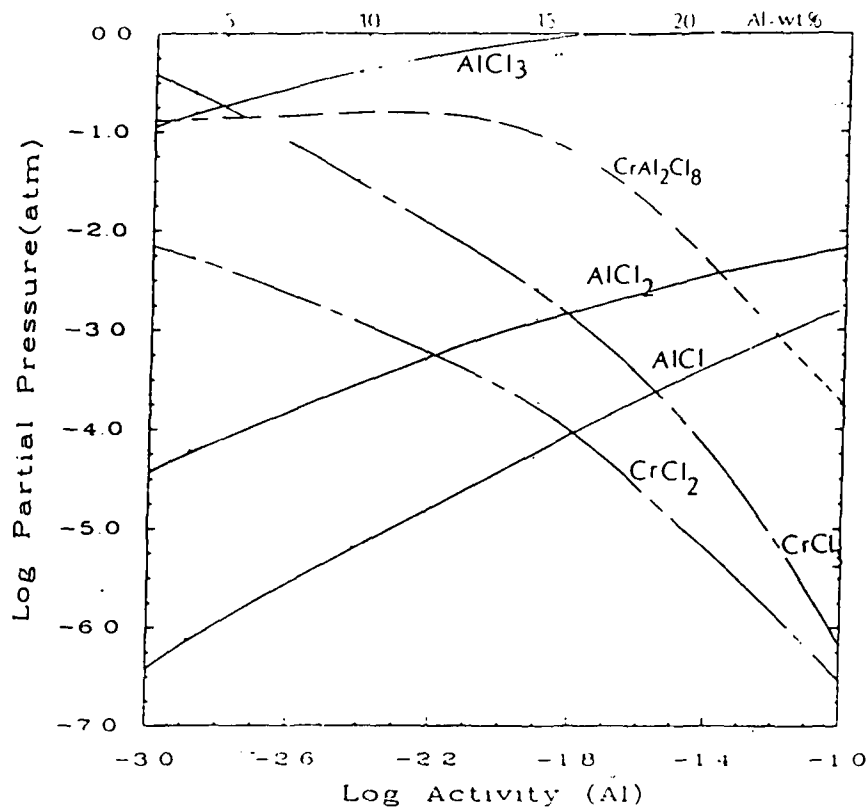


Figure 4: Equilibrium partial pressures of gaseous species in a CrCl_2 -activated pack as a function of Al-activity in the masteralloy (Ar atmosphere, 1273 K) (a) in the pack (b) at an Fe substrate.

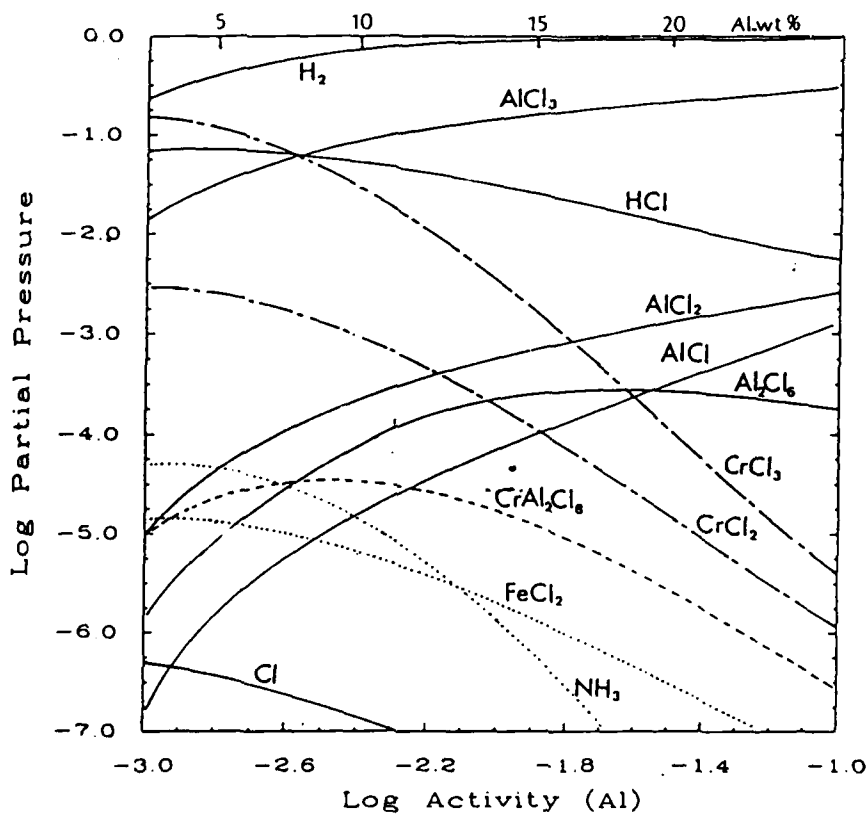
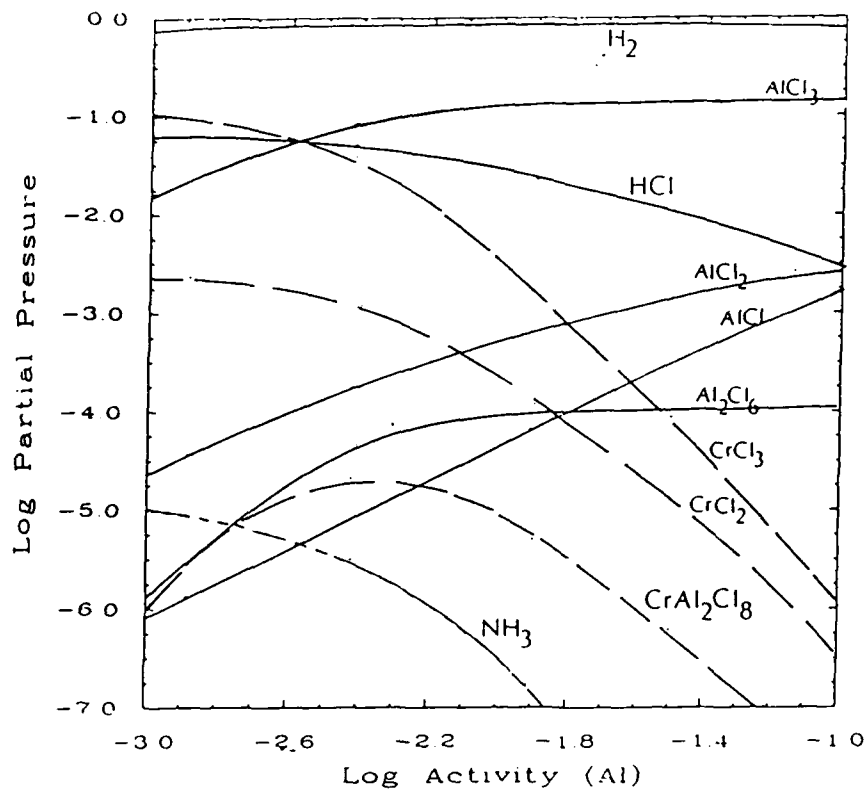


Figure 5: Equilibrium partial pressures of gaseous species in an NH₄Cl-activated pack as a function of Al activity in the masteralloy (Ar atmosphere, 1273 K) (a) in the pack (b) at an Fe substrate.

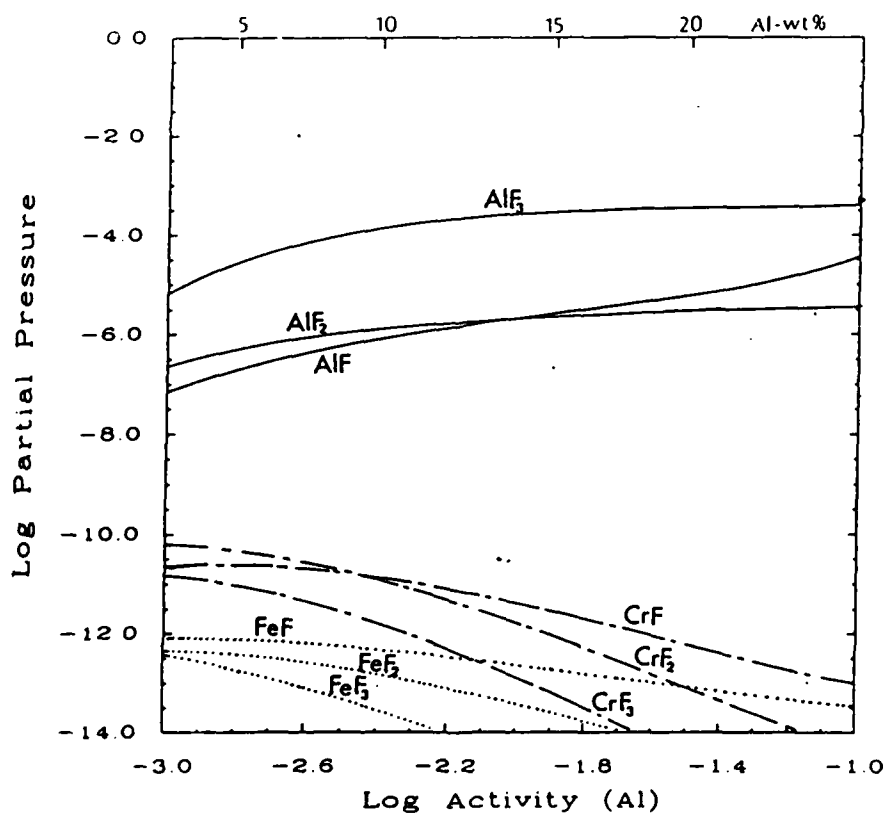
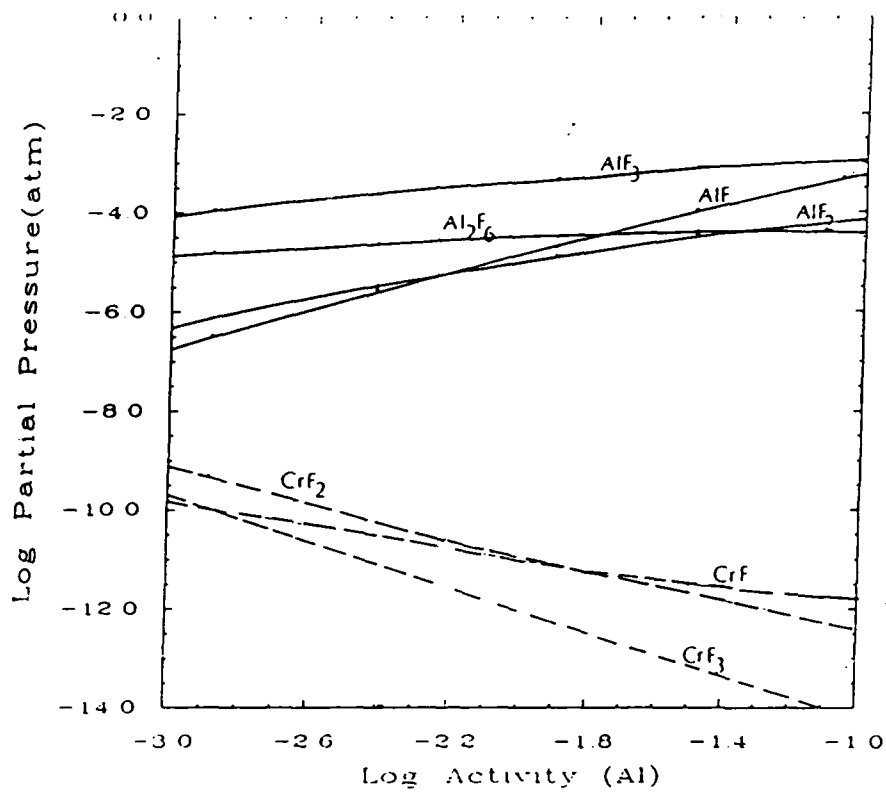


Figure 6: Equilibrium partial pressures of gaseous species in a NaF-activated pack as a function of the Al activity in the masteralloy (Ar atmosphere, 1273 K) (a) in the pack (b) at an Fe substrate.

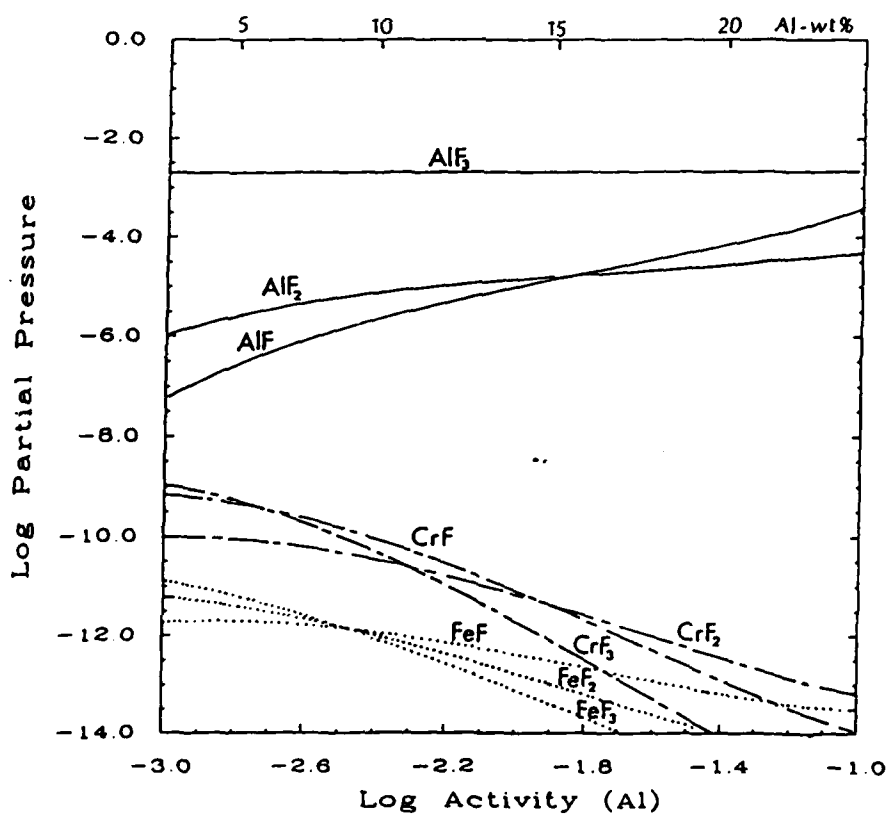
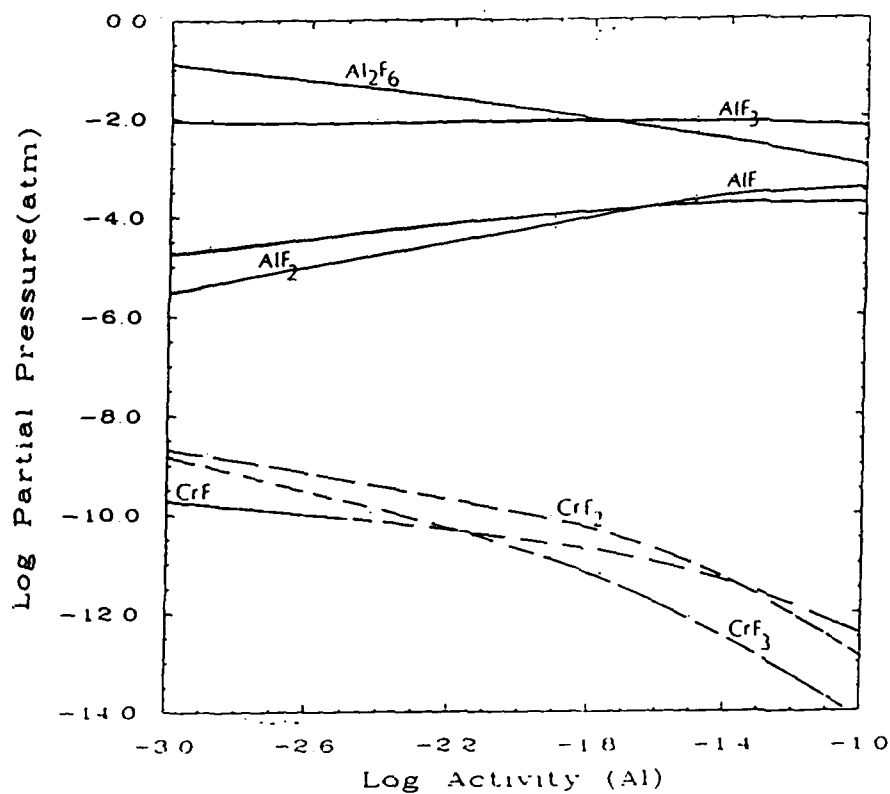
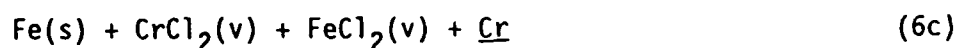
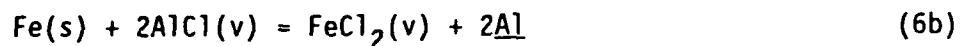
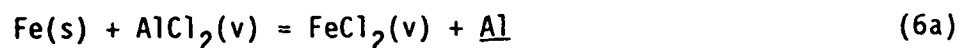


Figure 7: Equilibrium partial pressures of gaseous species in an AlF_3 -activated pack as a function of the Al activity in the masteralloy (Ar atmosphere, 1273 K) (a) in the pack (b) at an Fe substrate.

species relative to the aluminum species. These computations suggest the potential of the pack to aluminize or chromize as indicated by the absolute and relative magnitudes of the partial pressures of the Al and Cr halides. According to Fig. 3a, if NaCl were used as the activator, the codeposition of Al and Cr should be possible if the Cr-Al masteralloy contained between 13 and 10 wt% Al. In Fig. 3b, the partial pressure of FeCl_2 at an Fe substrate is quite high, which implies that exchange reactions such as



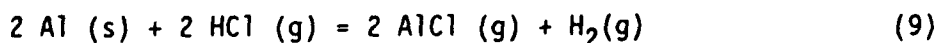
must be expected. Probably, each of these reactions is maintained in local equilibrium at an Fe/pack interface.

Figure 4a shows the equilibrium partial pressures of the metallic halides in a CrCl_2 -activated pack. Once again, at low Al activities, the CrCl_x partial pressures are higher than those of AlCl_x . Comparing Fig. 3a and 4a, the partial pressures of the CrCl_x and AlCl_x species in the CrCl_2 -activated pack are higher than those in the NaCl-activated pack. This results from the lower thermodynamic stability of condensed CrCl_2 compared to NaCl. The less stable CrCl_2 -activator stabilizes a higher P_{Cl_2} which favors CrCl_x formation in preference to AlCl_x . Not only are the magnitudes of the partial pressures of both the Cr and Al halides in the CrCl_2 pack higher than in the NaCl-activated pack, but the crossover occurs at higher activities of Al. Therefore codeposition should be possible for higher aluminum activities in the CrCl_2 pack than for the NaCl pack. The partial pressure of the ternary species CrAl_2Cl_8 is significant and could permit simultaneous Cr and Al transport. In Fig. 4b, the FeCl_2 pressure is also higher than in the NaCl pack, with crossovers occurring at higher Al contents in the masteralloy. The 2 wt% of CrCl_2 activator also provides a minor increase in the Cr content within the pack:



The NaCl-activated pack has no analogous contribution.

Figure 5a shows the results of calculations for a NH_4Cl -activated pack. The CrCl_x pressures are higher than in the NaCl-pack but lower than for the CrCl_2 packs and the crossover points occur at even higher Al activities. The rather low FeCl_2 pressures seen in Fig. 5b and the significant pressure of the ternary compound CrAl_2Cl_8 in Figs. 5a and b are to be noted. The ammonium chloride pack has the following additional reactions which may affect coating reactions:



Although AlN is a marginally stable phase, the formation kinetics are trivial.

Figures 6a and b and 7a and b indicate partial pressures in the pack and at the Fe substrate for NaF and AlF_3 -activated packs. In both the packs, the AlF_x partial pressures are higher than those for CrF_x and no crossovers occur. Therefore the use of fluoride-activated packs are unlikely to result in codeposition of Al and Cr. The partial pressures of the iron fluorides are also considerably lower than the iron chlorides implying that exchange reactions are negligible and iron-loss is minimized. The fluoride packs therefore tend to be strongly aluminizing even at low aluminum activities in the masteralloy.

Based on the results of the thermodynamic analyses, appropriate pack compositions can be predicted with chloride activators to achieve codeposition of Cr and Al. The activity of Al has to be very low ($\sim 10^{-3}$) relative to Cr to achieve comparable partial pressures of the halides. This Al activity corresponds to a quite Cr-rich binary Cr-Al alloy.

Based on the classification of Goward and Boone [18], this Al activity value would be in the "low aluminum activity" regime and would result in outward growing coatings as compared to the "high aluminum activity" regime ($a_{Al} = 1$) which results in inwardly grown coatings.

However, the Al activity in the low activity Al packs used by Goward and Boone was quite high ($a_{Al} = 0.35$) when compared to the present investigation. Pichoir's [19] low activity packs for "chromaluminizing" (85 Cr-15Al) did not result in codeposition possibly because the metal composition was not prealloyed. The proper choices of masteralloy composition and activator are very critical for achieving codeposition.

Walsh [3] points out that irrespective of whether the masteralloy is single phase or two-phase, no local depletion adjacent to the substrate occurs and that the gas phase composition in the pack and adjacent to the substrate is the same. Seigle [7] reported a much lower Al activity at the substrate surface than in the source alloy in aluminizing packs containing pure Al or Ni-Al masteralloys. This is a consequence of the depletion of both activator and coating element from the vicinity of the substrate. The activity of Al is unity for pure Al and quite high for Ni-Al binary alloys as compared to low Al activity Cr-Al alloys.

Figure 8a is the cross-section (optical micrograph) of a pure Ni coupon coated in a $CrCl_2$ -activated pack with a 95 Cr-5 w/o Al masteralloy for 25 hours at 1273 K in an inert argon atmosphere. Figure 8b shows the concentration profiles of Ni, Cr and Al from the surface of the coated substrate. The corresponding diffusion path is shown in Fig. 8c on an isothermal section at 1273 K of a Ni-Cr-Al equilibrium diagram [20]. The coating consists of a 2-phase Ni-rich γ + Cr-rich α outer layer and an inner, single phase Ni-rich face-centered-cubic γ . The absence of Kirkendall voids or pores is indicative of a good coating. Masteralloy or oxide particles from the pack have not been embedded in the substrate indicating that this coating was grown inward.

Figure 9a is the cross-section (optical micrograph) of a 2.25 Cr-1 Mo steel coated in a $CrCl_2$ -activated pack with 90Cr-10 Al masteralloy for 24 hours at 1308 K in an inert argon atmosphere. The coating contains a very thin fine-grained outer layer and an extensive inner layer with large columnar grains. The concentration profiles for Al and Cr through the coating are regular. The coating/substrate interface is marked by a step in the Cr concentration profile, corresponding to the γ loop in the Fe-Cr-Al system for 1308 K.

CONCLUSIONS

The thermodynamics of chromaluminization by a single step pack process have been analyzed. Appropriate pack compositions to obtain desired coating compositions can be predicted. Codeposition of Al and Cr can be achieved with chloride-activated packs over certain composition ranges of Cr-Al masteralloy, while fluoride-activated packs are strongly aluminizing

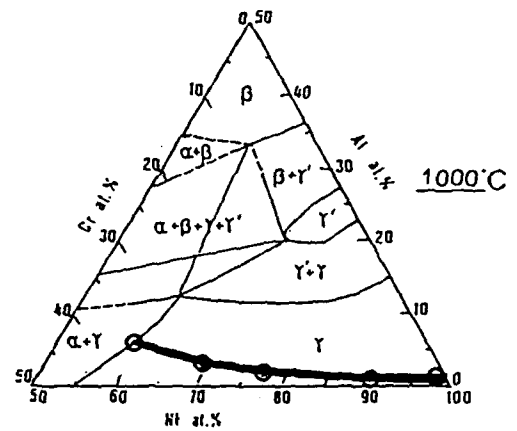
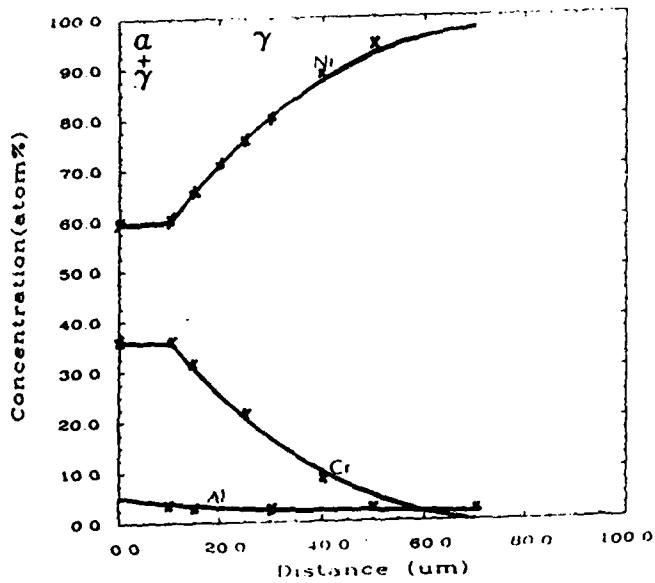


Figure 8: (a) Cross-section of pure Ni coated at 1273 K for 25 hours (CrCl_2), 95 Cr-5 Al, Ar) (b) Concentration profiles for Ni, Cr and Al for the coated sample (c) Corresponding diffusion path in the 1273 K section of the Ni-Cr-Al equilibrium diagram [20].

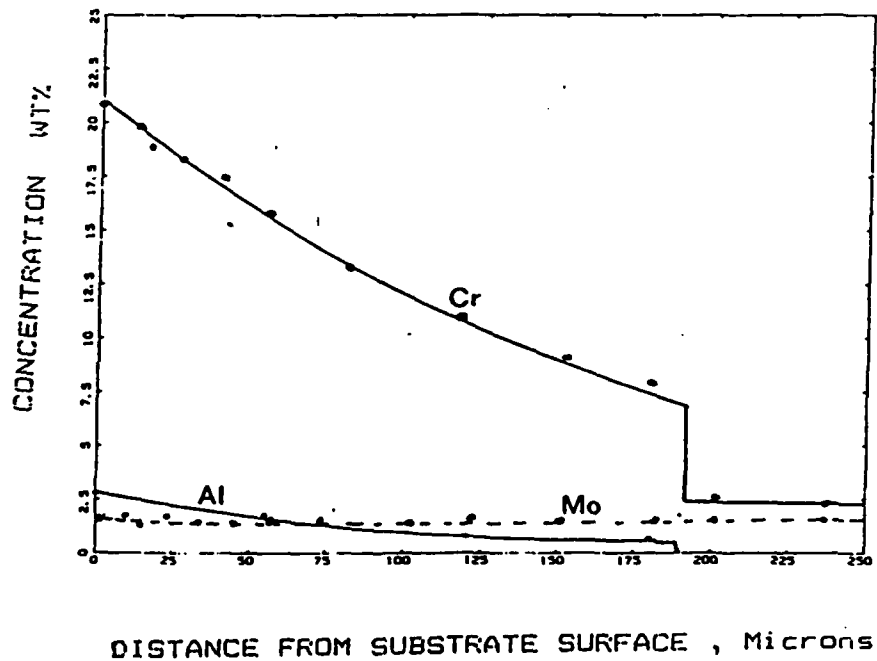
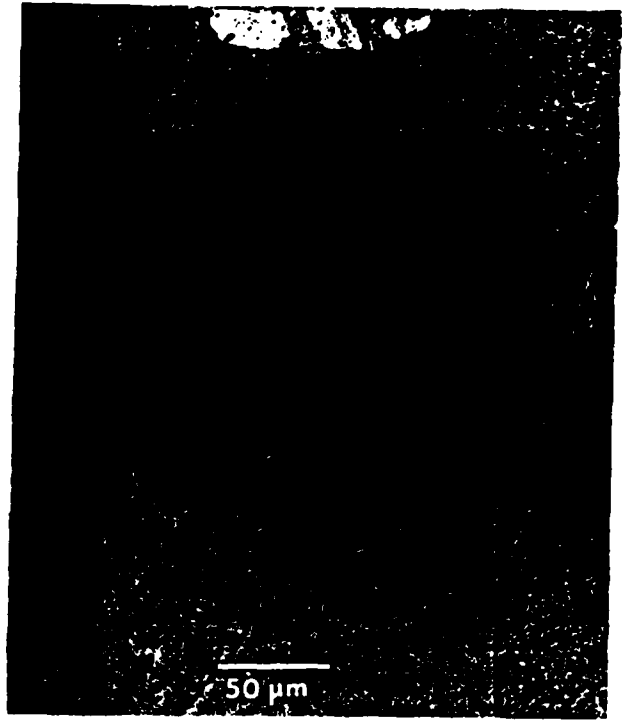


Figure 9: (a) Cross-section of 2-1/4 Cr-1 Mo steel coated at 1308 K for 24 hours (CrCl_2 , 90 Cr-10 Al, Ar) (b) Concentration profiles for Cr, Al and Mo.

even at low aluminum activities. Iron substrates generate significant FeCl_2 partial pressures while Ni substrates are almost non-reactive.

Effective coatings on Ni and 2.25 Cr-1 Mo steel substrates have been achieved, in nominal agreement with the thermodynamic predictions.

ACKNOWLEDGEMENTS

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