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## CHROMIZING-ALUMINIZING AND CHROMIZING-SILICONIZING COATING OF A FERRITIC STEEL

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**RESUME:** Des revêtements par diffusion simultanée de Cr-Al et Cr-Si ont été réalisés sur des aciers (Fe-12Cr) par le procédé de cementation activée. A l'aide d'un ordinateur, une étude thermodynamique de la phase gazeuse en équilibre avec le ciment a été développée. Le transport simultané de l'aluminium ou du silicium avec le chrome ne peut se justifier thermodynamiquement que grâce à l'emploi d'un ciment ayant une activité pour l'aluminium ou le silicium réduite de l'ordre de: respectivement  $10^{-3}$  et  $10^{-1}$  par rapport au Cr. Les résultats expérimentaux sur un acier ferritique sont en accord avec les prévisions. Les compositions obtenues permettent d'anticiper, une amélioration très substantielle de la résistance à l'oxydation et à la corrosion de l'acier. L'addition d'un élément réactif comme le titane pour améliorer l'adhérence de la couche d'oxyde, est discutée. La microstructure d'un revêtement Cr-Al dopé avec du titane est également présentée.

**ABSTRACT:** Simultaneous deposition of Cr-Al and Cr-Si as diffusion coatings for ferritic steel (Fe-12Cr) substrate have been carried out using the pack cementation method. A computer-assisted thermodynamic study of the equilibrium vapor pressures of volatile halide species formed by the pack components was performed. The simultaneous codeposition of Cr with Al is thermodynamically possible for chloride-activated packs when the activity of Al is about three orders of magnitude lower than the chromium activity; for Si-Cr codeposition, the activity of Si must be approximately one order of magnitude lower than that for Cr. The experimental tests of the theory agree reasonably with the predictions, and the resulting coatings promise an improvement in resistance to oxidation and corrosion. The simultaneous addition of Ti as an active element to improve oxide-scale adhesion is demonstrated for a Ti-doped Cr-Al coating.

### INTRODUCTION

Because of the presence of sulfur, chlorine, and other impurities in coal-derived environments at high temperatures, the metal components in coal utilization and coal conversion systems are subject to serious corrosion attack. Both ferritic and austenitic iron-base alloys are frequently employed in these coal-related applications.

Most high-temperature alloys or metallic coatings designed to withstand oxidizing environments rely on the formation of protective  $\text{Cr}_2\text{O}_3$  or  $\text{Al}_2\text{O}_3$  scales. However,  $\text{Cr}_2\text{O}_3$ -forming alloys are inadequate in such high temperature aggressive environments with high  $P_{\text{S}_2}$  and low  $P_{\text{O}_2}$  because  $\text{Cr}_2\text{O}_3$  is less stable thermodynamically and is susceptible to penetration or permeation to permit sulfide formation. Hsu [1] and Danyluk and Diercks [2] have shown that  $\text{Al}_2\text{O}_3$ -forming iron-base alloys are able to minimize the nucleation of fast-growing sulfides, such as FeS and CrS. Likewise,  $\text{SiO}_2$ -forming alloys are known to have excellent stress corrosion cracking and pitting resistance in aggressive aqueous environments [3].

Pack cementation is a relatively simple process which consists of surrounding the components to be coated in a powder mixture (pack) in a sealed or semi-sealed retort. This arrangement is heated in a protective atmosphere

to a high temperature, around 1000°C, for a sufficient period to form a diffusion coating. The pack typically consists of the substrate(s) to be coated, the masteralloy or coating element(s) source, an activator (usually a halide salt), and an inert filler (often alumina), to prevent the pack constituents from the sintering at high temperature. The pack cementation process is achieved and limited by two diffusion processes in series:

- First, the gaseous diffusion of halide species to (and from) the substrate for which the rate is decided by the difference in partial pressure for each different gas species in the pack and at the pack-substrate interface, and
- Second, diffusion in the solid substrate, where the rate dictates the depth of the coating and the surface concentrations for the coating elements.

In this presentation, experiments are reported for the simultaneous codeposition of Cr-Al and Cr-Si into a ferritic alloy (Fe-12Cr) from non-rotating packs. The resulting compositions and microstructures are discussed. Likewise, preliminary evaluations by thermodynamic calculations using the computer program SOLGASMIX-PV are reported. The vapor partial pressures of the different gas species in equilibrium with binary Cr-Al and Cr-Si masteralloys in the pack, in combination with a variety of activating salts, were calculated to assist in judging the feasibility of the process.

#### THERMODYNAMICS

Empirical attempts to deposit chromium-aluminum diffusion coatings by a static pack cementation process have not achieved complete control or satisfaction. Because the thermodynamic stabilities for the volatile halide species of chromium and aluminum differ greatly, the simultaneous codeposition of these two elements from a mixture of pure metallic powders in one isothermal step produces very aluminum-rich coatings even if the aluminum-content in the pack is small [4,5]. Recently, Rapp et al. [6] developed a procedure for the codeposition of Al and Cr simultaneously into pure Fe and a low steel alloy to achieve Kanthal-like surface compositions. Excellent isothermal oxidation resistance in air at 1000°C was provided by protective alumina scales. The coating process involved a Cr-rich Cr-Al masteralloy, a chloride activator salt, and a tumbling pack to minimize pack depletion.

For the case of codeposition of two alloying additions, thermodynamic equilibrium between the pack and metallic halide gas species must be considered. For a binary masteralloy source, the partial pressures of its metallic halides, which are generated by the following general reaction:



are a function of two variables: the activity of the metallic component in the masteralloy and the halide vapor pressure.

A microcomputer program, SOLGASMIX-PV, adapted by Besmann [7] was used to make the calculation. The equilibrium partial pressures of the gaseous species were calculated for various activator salts and different thermodynamic activities of the Cr-Al and Cr-Si components in binary masteralloys.

#### Simultaneous Codeposition of Cr-Al.

Details of the calculation process and the results of SOLGASMIX calculations of the equilibrium vapor pressures as a function of Cr-Al masteralloy compositions have been published previously for a variety of activator salts [8]. Only the most important results are described here.

Almost four orders of magnitude exist between the aluminum and chromium halide vapor pressures when pure Al and Cr powders ( $a_{Al} = a_{Cr} = 1$ ) are

equilibrated in a pack activated by NaCl; thus an alloy with a very low Al activity compared with the Cr activity must be used. For the 90Cr-10m/o Al binary alloy, the activity of aluminum is about three orders of magnitude lower than the activity of chromium [9]. Therefore, a range of reasonable masteralloy compositions does exist where the vapor pressures of  $AlCl_x$  and  $CrCl_x$  can be comparable, depending upon the proper choice of activator salt.

Figures 1 and 2 present the partial pressures of the gaseous species as a function of the Al activity in  $CrCl_2$ - and  $AlF_3$ - activated packs. Figure 1 shows that  $AlCl_x$  ( $x=1,2$ ) and  $CrCl_2$  partial pressures are comparable for Cr-Al binary masteralloys with compositions corresponding to 13-16 wt% Al. If a local equilibrium exists at the interface of the pack and an Fe substrate, the same calculations can be done. The results indicate that the partial pressure of  $FeCl_2(v)$  is quite high; therefore displacement reactions with the substrate must be expected to lead to a loss of Fe via  $FeCl_2(v)$ . In Figure 1, the vapor pressure of  $CrAl_2Cl_8$  is also very high, and this species may contribute to codeposition of Al and Cr. The calculations reported in Fig. 1 show that the acceptable composition range for the masteralloy is quite limited, so that trial and error methods would not identify the proper conditions efficiently.

If a fluoride activator salt were used, the  $AlF_x$  partial pressures are always higher than those of  $CrF_x$  even for a very low Al concentration (Figure 2). Identical results were obtained with a NaF-activated pack. Therefore, fluoride-activated packs can only aluminize a substrate. Other calculations have shown that the use of hydrogen, rather than argon, as a background gas generates a halogen activity which is too low to permit Cr and Al codeposition, even for chloride activators.

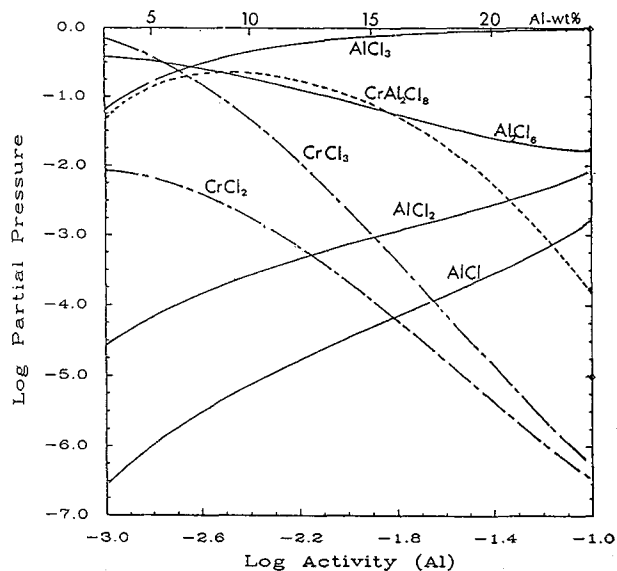
#### Codeposition of Chromium and Silicon

Thermodynamic calculations were also performed for 1273K in an argon background atmosphere for various activators and masteralloys. The activities of Cr and Si are extrapolated from reference [10] and [11] and are reported in Table I. Identical procedures as described in the reference [9] were used. The volatile halides of silicon are thermodynamically more stable than those of chromium. Therefore to achieve a chromium-rich Cr-Si coating, the silicon activity in a binary Cr-Si masteralloy in the pack must be reduced to generate comparable Cr and Si halide partial vapor pressures.

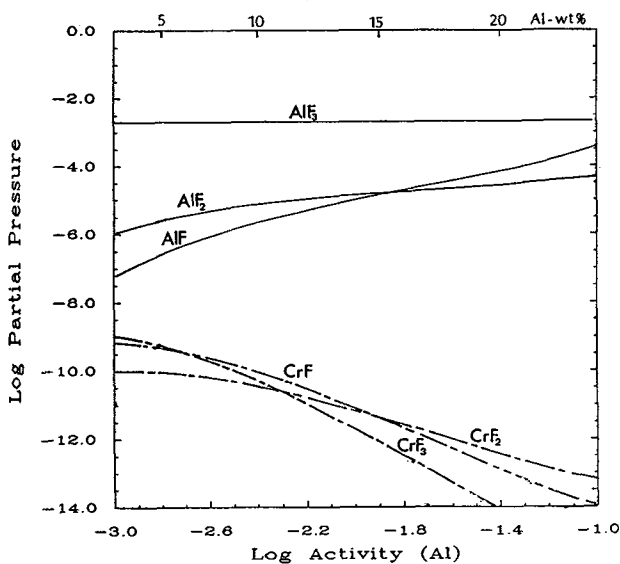
Table I: Activities of Cr and Si in Cr-Si Alloys at 1273K

Phase Field	wt% Si	$-\log a_{Si}$	$-\log a_{Cr}$
Cr+Cr <sub>3</sub> Si	3.3/13.2	4.14	0.27
Cr <sub>3</sub> Si+Cr <sub>5</sub> Si <sub>3</sub>	15.2/23.5	1.99	0.98
Cr <sub>5</sub> Si <sub>3</sub> +CrSi	26.4/35.0	0.96	1.61

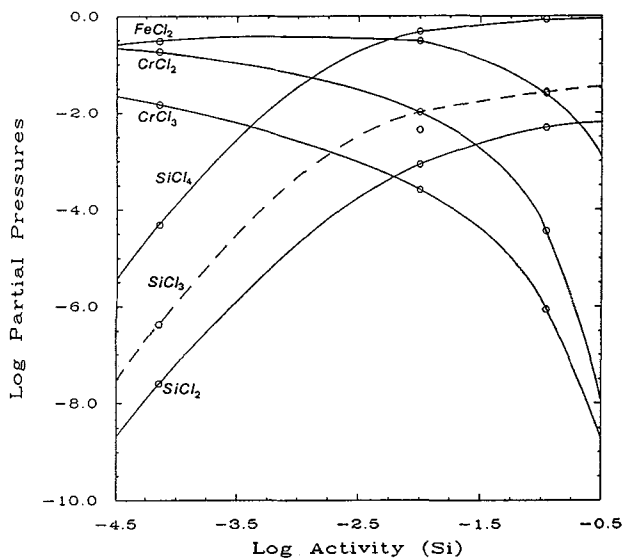
Figure 3 presents calculated partial pressures in the pack for  $FeCl_2$ -activated packs as a function of the Si activity in a Cr-Si masteralloy. The partial pressures of  $CrCl_2$  and  $SiCl_2$  are of the same order of magnitude for a Cr<sub>3</sub>Si-Cr<sub>5</sub>Si<sub>3</sub> two-phase alloy. Computations for packs activated by the more stable salt NaCl do not show a crossover for  $SiCl_x$  and  $CrCl_x$  partial pressures compatible with the use of a two-phase alloy. Calculations of vapor pressures in the pack and at the substrate interface indicate a vapor pressure for  $FeCl_2$



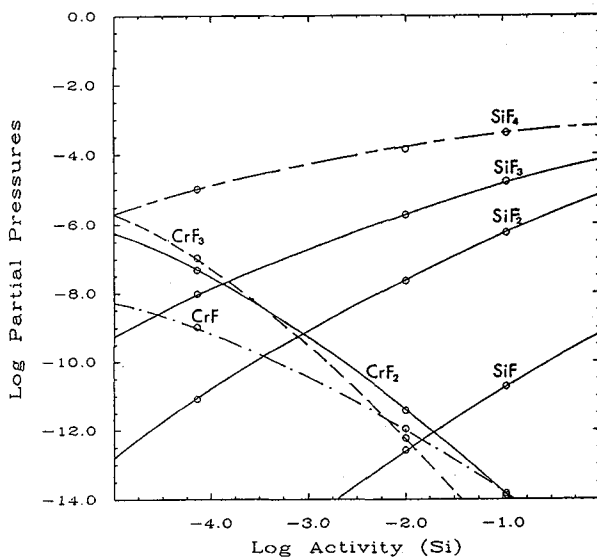
**Figure 1:** Equilibrium partial pressure of gaseous species in a CrCl<sub>2</sub>-activated pack as a function of Al-activity in the Cr-Al masteralloy (Ar atmosphere, 1273 K).



**Figure 2:** Equilibrium partial pressures of gaseous species in an AlF<sub>3</sub>-activated pack as a function of the Al activity in the Cr-Al masteralloy (Ar atmosphere, 1273 K).



**Figure 3:** Equilibrium partial pressure of gaseous species in a  $\text{FeCl}_2$ -activated pack as a function of Si activity in the Cr-Si masteralloy (Ar atmosphere, 1273 K) Data points indicate values for two-phase fields.



**Figure 4:** Equilibrium partial pressures of gaseous species in a  $\text{AlF}_3$ -activated pack as a function of Si activity in the Cr-Si masteralloy (Ar atmosphere, 1273 K) Data points indicate values for two-phase fields.

higher than the other metallic chloride species. However, because the pack is activated by  $\text{FeCl}_2$ , an excessive loss of  $\text{FeCl}_2$  from the substrate should not be experienced.

According to Figures 3 and 4, the volatile chromium halides have much lower vapor pressures in a NaF-activated pack than in a  $\text{FeCl}_2$ -activated pack. Therefore, simultaneous codeposition of Cr and Si using a NaF-activated pack can only be expected with the more Cr-rich Cr-Si masteralloy. Obviously, the process temperature offers a third variable to achieve flux balances in the pack.

## EXPERIMENTAL RESULTS AND DISCUSSION

### Chromizing-Aluminizing

Cementation packs of different compositions deduced from thermodynamic predictions have been used to coat a ferritic Fe-12Cr steel; a few of these coatings are reported here.

Figure 5 presents the cross-section metallography and the corresponding Cr and Al concentration profiles for the coating, using a 92Cr-8wt%Al masteralloy at 1000°C for 16 hours. The activator was a mixture of  $\text{AlCl}_3$  and NaCl. Aluminum trichloride sublimes at 450K and provides a very high chloride activity at the beginning of the process. The presence of the condensed phases NaCl(l) or  $\text{NaAlCl}_4$ (l) provides a more moderate chlorine activity and stabilizes the process at high temperature. In Figure 5, absence of both pack entrapment at the surface and Kirkendall voids in the interior indicates that the coating grows essentially by inward diffusion of Cr and Al. Beneath a thin external layer of alpha Cr (with 15 wt% Fe in solution), the composition is approximately 25 wt%Cr and 5 wt%Al. For a 90Cr-10Al masteralloy with a higher aluminum activity and the same activator, the formation of the outer alpha layer was avoided, but analyses of the surface indicated a reduction in the Cr content, (11 wt%Cr with 9 wt% Al).

The codeposition of Cr and Al is particularly successful for this ferritic steel. The combined contents of Cr and Al at the coating surface are compatible with the formation of a compact and regular alumina scale during exposure to an oxidizing or high temperature corrosive environment. However, to enhance the adherence of the oxide scale, additional treatments were conducted to study the feasibility of adding a reactive element during the Cr-Al codeposition process. Many studies have shown that oxidation-resistant iron-base alloys containing 1 wt% or less of yttrium, hafnium or titanium exhibit excellent cyclic oxidation resistance.

### Doping with Active Element

To achieve the addition of a third element during a simultaneous codeposition of Cr-Al, two conditions must be met. First, the additional element should enjoy a reasonable solubility in the substrate to be coated. For an iron alloy substrate, the elements Y, Hf and Ti each exhibit a solubility compatible with the desired range of composition. Second, the element should not coexist in the pack as a pure metallic phase which would compete favorably with Cr and Al in the formation of volatile halides. Therefore, the coating systems which can permit a doping of the coating are limited. A ternary alloy, Cr-Al-X (X denotes the active element) could be used as a masteralloy. However, the addition of the active element solute, even if it were soluble in the Cr-Al alloy would introduce an unknown activity for the additive element. Actually, the most convenient solution is to add the element to the pack in its oxide form.

Titanium-doping a Cr-Al coating was achieved for the ferritic Fe-12Cr steel substrate. Titanium was introduced to the pack by mixing 5 wt% of  $\text{TiO}_2$  powder (1 to 5 microns) into the pack. This oxide was chosen because Ti

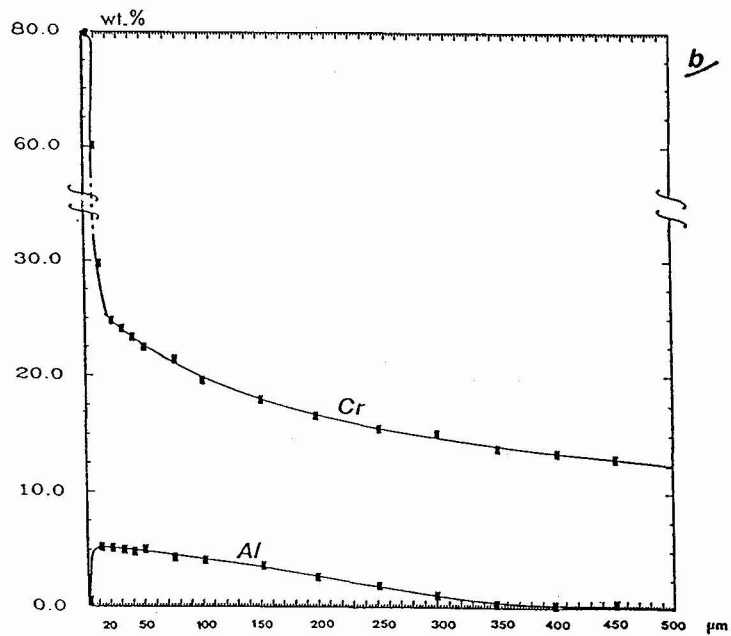
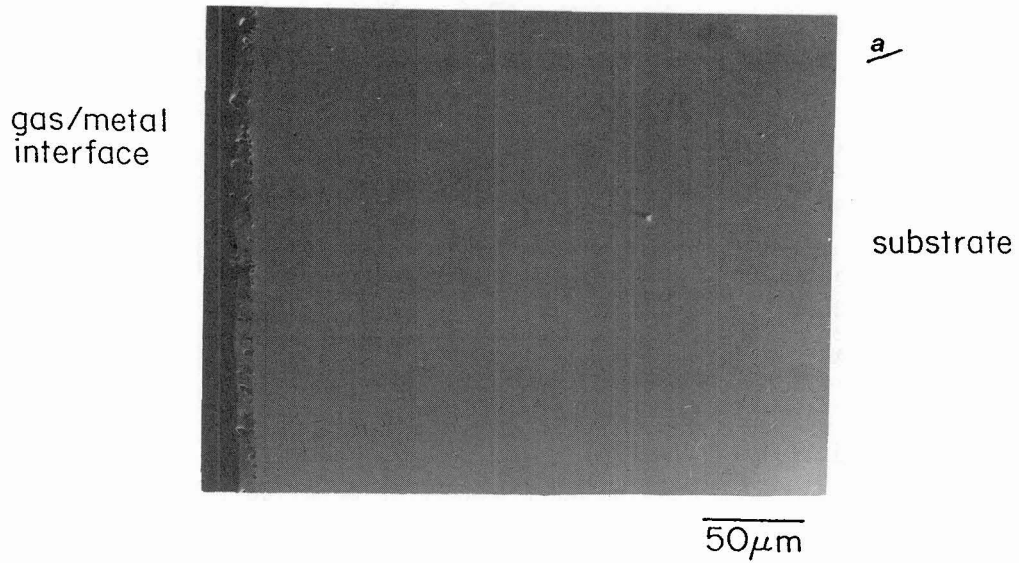
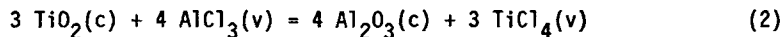


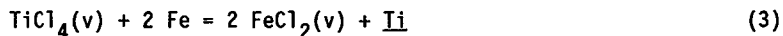
Figure 5: (a) Cross-section by SEM of Fe-12Cr Steel Coated at 1050C for 16 hours ( $\text{AlCl}_3\text{-NaCl}$ , 92Cr/8Al, Ar). (b) Concentration Profiles for Cr and Al.



provides a quite high  $\text{TiCl}_4$  vapor pressure and moderate oxide stability. From a reaction involving  $\text{AlCl}_3(\text{v})$ ,



the titanium chloride vapor pressure is on the order of  $10^{-6}$  atm for an  $\text{AlCl}_3$  pressure of 1 atm. By an exchange reaction with the surface,



titanium can be introduced into the substrate.

Figure 6a is the cross-section (SEM micrograph) of a ferritic Fe-12Cr steel coated in a  $\text{AlCl}_3 + \text{NaCl}$ -activated pack with a 90Cr-10Al masteralloy for 19 hours at 1310K. The coating is free of pores, with no particle entrapment. The composition of the coating, 5 microns below the outer surface, is Fe-17Cr-4Al-0.4Ti(wt%). At the surface, titanium was also detected in the coating by the presence of fine titanium-rich particles, see Figure 6b. These, are probably fine titanium intermetallics formed upon cooling the coating.

#### Chromizing-Siliconizing

Figure 7 presents the cross-section metallography and the corresponding Cr and Si concentration profiles for the coating of a ferritic Fe-12Cr steel using a  $\text{FeCl}_2$ -activated pack at 1303 K for 24 hours. The masteralloy was a 2-phase mixture of  $\text{Cr}_3\text{Si} + \text{Cr}_5\text{Si}_3$ . The interdiffusion layer is pore-free and no pack entrapment was observed. An outer layer rich in chromium had a thickness of less than 20 microns, and it was separated from the substrate by a continuous line of fine porosity. The underlying interdiffusion layer of 140 microns had a composition of Fe-15Cr-6Si (wt%) at its external surface. This coating was a result of a first attempt at chromizing-siliconizing, and future work should avoid the external layer and optimize the composition of the interdiffusion zone.

#### CONCLUSIONS

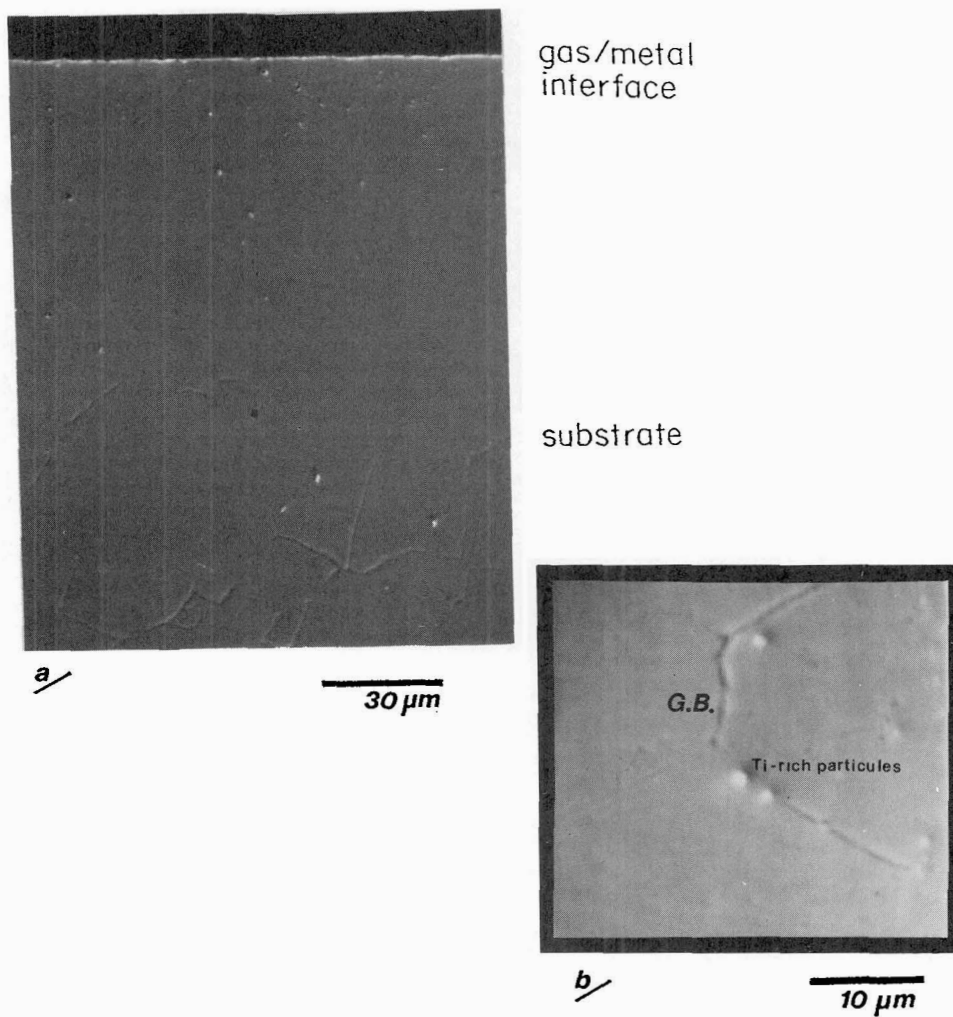
Codepositions of Cr-Al and Cr-Si into an iron-base Fe-12Cr alloy were carried out by the pack cementation process. However, such codepositions can be achieved only for very specific, limited combinations of conditions. Computer assisted thermodynamic calculations of the equilibrium vapor pressures for given binary masteralloys and given halide salts can assist in identifying the necessary pack compositions. Surface concentrations of approximately 25Cr-5Al and 15Cr-6Si (wt%) were deposited on the ferritic Fe-12Cr steel. These compositions are expected to form protective alumina and silica scales that would resist high temperature corrosion and oxidation. Doping of the Cr-Al coating with about 0.4wt% Ti was also demonstrated.

#### ACKNOWLEDGEMENT

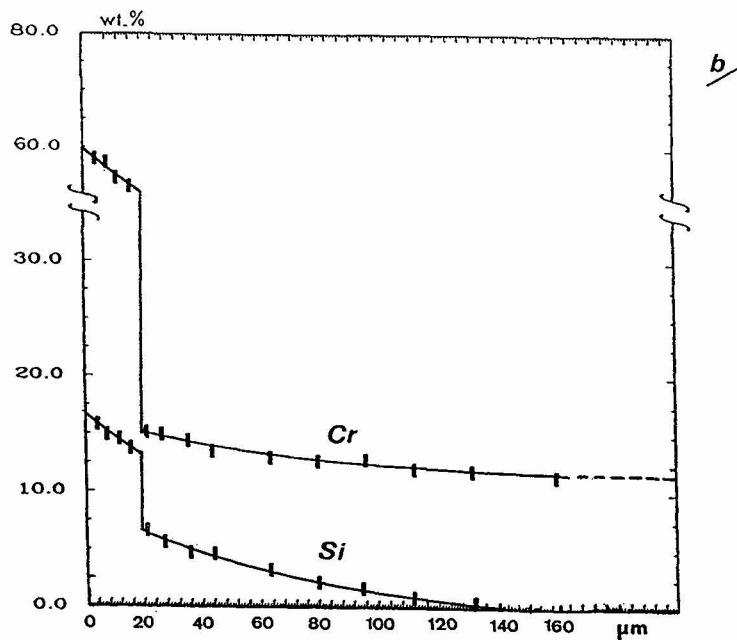
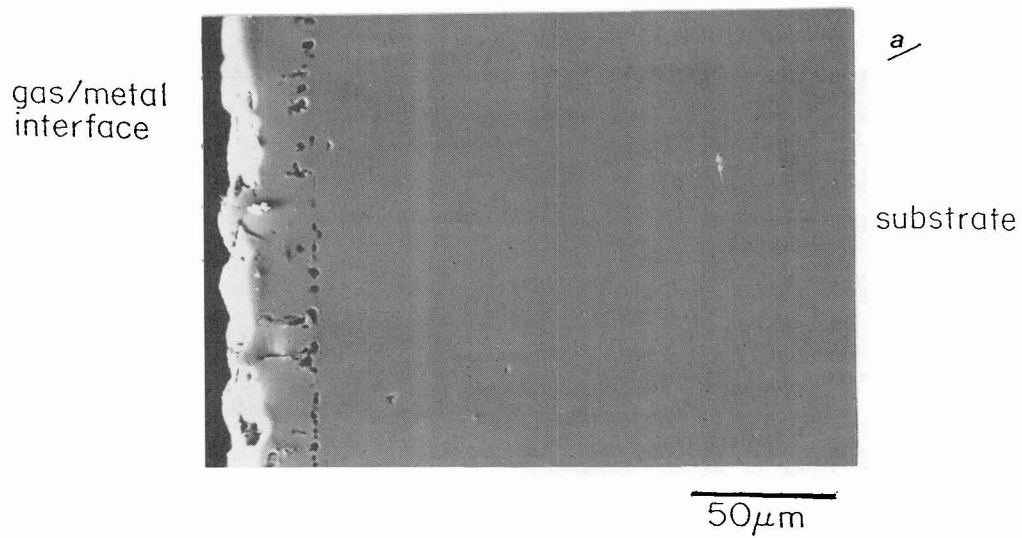
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**Figure 6:** (a) Cross-section by SEM of Fe-12Cr Steel Coated at 1310 K for 19 hours ( $\text{AlCl}_3$ -NaCl, 90Cr/10Al,  $\text{Al}_2\text{O}_3 + \text{TiO}_2$ , Ar). (b) high magnification view of the external region.



**Figure 7:** (a) Cross-section by SEM of Fe-12Cr Steel Coated at 1303 K for 24 hours, using a  $\text{FeCl}_2$  activator and a  $\text{Cr}_5\text{Si}_3 - \text{CrSi}$  masteralloy. (b) Concentration Profiles for Cr and Si.

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