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## ON THE KINETICS OF PACK ALUMINIZATION

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ABSTRACT

A theory of pack aluminization has been formulated by combining gaseous and solid-state diffusion rates. This theory relates the surface composition of the coating and therefore, in principle, the phase morphology and the growth rate of the coating, to pack operating parameters such as pack Al density, type of activator, temperature and others. Experimental data on the aluminization of unalloyed Ni in pure Al packs obtained by us to date are in good agreement with the predictions of the theory.

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## ON THE KINETICS OF PACK ALUMINIZATION

### Introduction

The pack aluminization process is extensively used to form protective coatings on superalloy components of aircraft gas turbines. In this process the metal to be coated is placed in a powder mixture consisting essentially of Al, a halide activator such as NaF, and an inert filler material such as  $\text{Al}_2\text{O}_3$ . Other metals such as Ni, Cr, Si, Ti are sometimes added (1, 2) to control the Al activity or otherwise influence the properties of the coating. During aluminization, Al is transferred from the pack to the specimen surface in the form of aluminum halides. These compounds decompose at the surface to release Al which diffuses into the metal, creating the Al-rich coating. The aluminization process thus involves three steps: 1) gaseous diffusion, 2) surface reaction and 3) solid diffusion. Of these three it is assumed that the surface reaction step is rapid and the kinetics of the process is governed by a combination of gaseous diffusion in the pack and solid state diffusion in the coating. The gaseous diffusion step was recently analyzed by Levine and Caves (3). In the following a quantitative description of the kinetics of aluminization is given which takes diffusion in the solid as well as the gas phase into account.

### Kinetics of Pack Aluminization

A. Gaseous Diffusion: Levine and Caves' (3) model which applies to packs containing unalloyed Al, assumes that aluminum is transferred from the pack to the coating surface by the diffusion of aluminum halides through an Al-free zone in the pack adjacent to the specimen surface.

In the body of the pack, the halide vapor pressures are taken as those in equilibrium with the bulk pack composition. The halide vapor pressures at the specimen surface, which is assumed to be at a constant Al activity, are determined by mass-balance and thermodynamic equilibrium conditions at this surface. Chemical reactions are assumed to occur rapidly enough at the pack-coating interface to allow the establishment of a local equilibrium.

As Al is transformed from the pack to the specimen surface it is assumed that the width of the depleted zone and consequently the diffusion distance for the halide vapor increases. This leads to a parabolic relationship between the weight of Al transferred  $W_g$ , in gms./cm<sup>2</sup> and time,  $t$ , in seconds,

$$W_g^2 = \frac{2\rho\epsilon M}{\ell} \frac{N_{Al}d}{A} t = K_g t \quad (1)$$

in which  $\epsilon$  and  $\ell$  are correction factors for pack porosity and pore length,  $M$  is the atomic weight of Al,  $\rho$  is the pack Al concentration in gms/cm<sup>3</sup>,  $d$  is the diffusion distance in cm,  $A$  is the total area in cm<sup>2</sup>, and  $N_{Al}$  is the overall rate of diffusion of Al through the gas phase in moles/sec.

The instantaneous flow of Al through the gas phase is given by

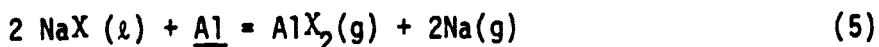
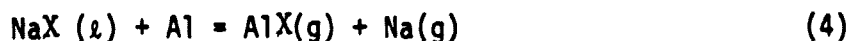
$$\frac{N_{Al}d}{A} = \frac{1}{RT} \sum_i D_i (P_i - P_i') \quad (2)$$

where  $D_i$  is the diffusivity,  $P_i$  and  $P_i'$  are the partial pressures of the  $i^{th}$  Al-bearing species in the pack and at the coating surface, respectively,  $T$  is the temperature and  $R$  the gas constant. Hence the parabolic rate constant,  $K_g$ , is given by

$$K_g = \frac{2\rho\epsilon M}{\ell RT} \sum_i D_i (P_i - P_i') \quad (3)$$

Application of the above equations involves calculation of the equilibrium pressures  $P_1$  and  $P_1'$ . The method of calculation depends upon pack operating conditions and type of activator used.

The pack aluminization process is generally carried out at atmospheric pressure by placing a semi-open retort with the pack and the parts to be coated in a flowing  $H_2$  or inert atmosphere. The activators in common use can be divided into two classes. The sodium halides i.e.,  $Na(F, Cl, Br, I)$  as well as  $AlF_3$  remain in the pack as condensed phases at the usual activator ratios ( $1-10^W/o$ ) and pack cementation temperatures ( $800-1100^{\circ}C$ ). If  $NH_4F$  or  $NH_4F.HF$  are used as activators, crystalline  $AlF_3$  forms in the pack by reaction with aluminum. With the highly volatile activators  $Al(Cl, Br, I)_3$  and  $NH_4(Cl, Br, I)$ , no condensed phase is formed in the pack. The composition of the gas-mixture that forms in the pack will be unstable because of continuous losses. While the function of both kinds of activators is qualitatively identical, only the former class can be quantitatively analyzed. The composition of the gas phase can be calculated given the temperature, aluminum activity and the total pressure. For  $NaX$ , the partial pressure ( $p_1$ ) of the significant species in the bulk pack will be given by the equilibrium constants of the following chemical reactions, subject to the last two conditions:

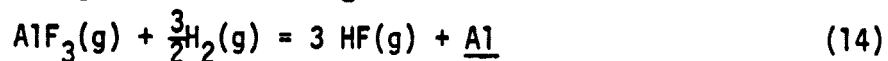




$$P_{\text{Na}(g)} = 3 P_{\text{AlX}_3(g)} + 6 P_{\text{Al}_2\text{X}_6(g)} + 2 P_{\text{AlX}_2(g)} + P_{\text{AlX}(g)} + P_{\text{HX}(g)} \quad (10)$$

$$\sum P_i = 1 \text{ atm.} \quad (11)$$

For  $\text{AlF}_3$  or ammonium fluoride activators, the partial pressure of  $\text{AlF}_3(g)$  equals the vapor pressure of  $\text{AlF}_3(g)$  and is independent of the aluminum activity. The other partial pressures can be calculated from:



$$P_{\text{AlF}_3(g)} + P_{\text{AlF}_2(g)} + P_{\text{HF}(g)} + P_{\text{H}_2(g)} = 1 \text{ atm.} \quad (15)$$

Similar calculations for  $P_i$  at the specimen surface must take into account certain kinetic considerations. The pack gases not only transport Al, but also halogen, hydrogen and sodium gas. For the NaX activators, Na(g) and halogen must be transported in equimolar proportions, so that they react and condense back into NaX(l) near the specimen surface.

Therefore, eq. (10) is modified to:

$$D_{\text{Na}}(P_{\text{Na}} - P'_{\text{Na}}) = 3 D_3(P_{\text{AlX}_3} - P'_{\text{AlX}_3}) + 2 D_2(P_{\text{AlX}_2} - P'_{\text{AlX}_2}) + D_1(P_{\text{AlX}} - P'_{\text{AlX}}) + D_{\text{HX}}(P_{\text{HX}} - P'_{\text{HX}}) + 6 D_6(P_{\text{Al}_2\text{X}_6} - P'_{\text{Al}_2\text{X}_6}) \quad (16)$$

For  $\text{AlF}_3$ , since its vapor pressure must be constant throughout the pack, a part of the Al that is carried by AlF and  $\text{AlF}_2$  to the specimen surface is lost due to formation of  $\text{AlF}_3(s)$ , for example:  $3\text{AlF}(g) = \text{AlF}_3(s) + 2 \text{Al}$ .

This implies that the actual Al transfer equation should be:

$$W_g^2 = \frac{2\rho M_e}{RT} [(2/3) \cdot D_1 \cdot (P_{\text{AlF}} - P'_{\text{AlF}}) + (1/3) \cdot D_2 \cdot (P_{\text{AlF}_2} - P'_{\text{AlF}_2})] \cdot t \quad (17)$$

In principle, a  $H_2$  balance equation should be incorporated, but has been found to be practically unimportant. The Al deposition rate constant,  $K_g$ , has been computed at  $800^\circ\text{C}$  and  $1093^\circ\text{C}$  for NaCl, NaF, NaI and  $AlF_3$  as a function of specimen surface composition. The Al activity as a function of composition in the Ni-Al system (4) and thermochemical data (5) are available in the literature. The gas diffusivities and the value of  $\lambda = 4$  were taken from Levine and Caves' paper (3). The pack compositions we selected corresponded to  $\rho = 0.04 \text{ gm/cm}^3$  and porosity,  $\epsilon = 0.70$ .

B. Solid Diffusion: If the surface of the specimen remains at constant composition, assuming that diffusion takes place into an infinitely extended medium, the rate of diffusion in the solid will also obey a parabolic law expressed by the equation

$$w_s^2 = K_s t \quad (18)$$

where  $K_s$ , the parabolic rate constant for diffusion in the solid, will depend upon the value of the surface composition. It is evident that in order for the composition at the surface of the coating to be time invariant, the  $K$  values must be identical, i.e., the surface composition must assume that value for which  $K_s = K_g$ . This unknown value of surface composition can be predicted if  $K_s$ , as well as  $K_g$ , can be calculated.

For complex superalloys, the necessary diffusivity and thermodynamic data are not yet available to carry out the calculation of  $K_s$ . Sufficient data are available for the binary Ni-Al system, however, to permit calculation of the  $K_s$  values for the aluminization of unalloyed Ni.



The aluminide coating on nickel will consist of single-phase intermetallic layers of progressively decreasing Al content, such as  $\text{Ni}_2\text{Al}_3$ ,  $\text{NiAl}$ ,  $\text{Ni}_3\text{Al}$  and the  $\text{Ni(Al)}$  terminal phase. The identity of the first layer is determined by the surface composition. The position of the interface between any two layers  $i$  and  $j$  is given by:

$$x_{ij} = p_{ij} \sqrt{t} \quad (19)$$

The free surface of the coating also moves outward parabolically with time, because Al is gained but Ni not lost in pack aluminization (6). The thickness of the layer  $j$  is:

$$t_j = (p_{ij} - p_{jk}) \sqrt{t} = q_j \sqrt{t} \quad (20)$$

The growth rates of the various layers, as well as of the coating as a whole are known if the constants  $p_{ij}$  can be calculated. These depend on the interdiffusion coefficients and the composition parameters of the various phases.

The first step in calculating  $p_{ij}$  is to set up material balance equations at the interfaces. Thus, the rate of movement of the  $ij$  interface is given by:

$$(c_{ij} - c_{ji}) (dx_{ij}/dt) = -D_i (\partial c_i / \partial x)_{ij} + D_j (\partial c_j / \partial x)_{ij} \quad (21a)$$

$c_{ij}$  and  $c_{ji}$  are the equilibrium compositions, in atom fraction, of the phases  $i$  and  $j$ , respectively, at the interface  $ij$ . For a surface composition  $c_s$ , the material balance equation for the free coating surface i.e., the vapor-solid interface,  $s$ , is:

$$(1 - c_s) (dx_s/dt) = D_j (\partial c_j / \partial x)_s \quad (21b)$$

If the interdiffusion coefficients  $D_i$  do not vary with composition, then analytical solutions are known (7,8) for the composition profile in each phase, for instance the solution for the phase  $j$  is:

$$c_j(x,t) = c_{ji} - (c_{ji} - c_{jk}) \cdot \frac{\text{erf}(x/2\sqrt{D_j t}) - \text{erf}(p_{ij}/2\sqrt{D_j})}{\text{erf}(p_{jk}/2\sqrt{D_j}) - \text{erf}(p_{ij}/2\sqrt{D_j})} \quad (22)$$

With the help of these and eq. (19), all the derivatives in eq. (21a,b) can be replaced, and a system of  $n$  equations in  $n$  unknowns,  $p_{ij}$ , where  $n$  is the total number of phases in the coating, can be generated and solved. This analytical scheme suffices in many practical cases of binary diffusion. In the Ni-Al system, however, it has been found that while  $\text{Ni}_2\text{Al}_3$ ,  $\text{Ni}_3\text{Al}$  and the Ni(Al) terminal solution have diffusivities practically invariant with composition, the interdiffusion coefficient in NiAl varies strongly with composition (9). It has a minimum at around the equiatomic composition, and on either side of this composition,  $D$  varies exponentially:

$$D_{\text{NiAl}} = D_0 \exp(\beta c) \quad (23)$$

For such a case, an analytical solution is not known. Therefore, the composition profile in NiAl has to be computed numerically. This is done by first transforming the diffusion equation in NiAl:

$$(\partial c / \partial t) = \partial / \partial x [D (\partial c / \partial x)] \quad (24)$$

to an ordinary differential equation:

$$y(d^2y/dz^2) + (p_{12}^2/2 D_0) z (dy/dz) = 0 \quad (25)$$

by substitution of the new variables:

$$y = \exp(\beta c) \text{ and } z = (x/p_{12}\sqrt{t}) \quad [p_{12} = \text{rate const. for the NiAl/Ni}_3\text{Al interface}]$$

The transformed eq. (25) can be solved by a numerical procedure described in detail in Ref (8). In Fig. 2, we show a number of concentration profiles across NiAl-Ni<sub>3</sub>Al-Ni(Al) terminal solution type of coatings, numerically computed for 20 hours of pack cementation at 1100°C. The numerical method becomes important only when NiAl is the surface layer

of the coating. If the surface composition is such that  $\text{Ni}_2\text{Al}_3$  is the first layer, then we have found that all the other layers develop relatively small thicknesses. In these cases, a constant value of the interdiffusion coefficient for  $\text{NiAl}$ , obtained by averaging the  $D$  over its homogeneity range, can be used in the analytical scheme to give accurate enough results for  $\text{Ni}_2\text{Al}_3$ - $\text{NiAl}$ - $\text{Ni}_3\text{Al}$ - $\text{Ni(Al)}$  type of coatings.

Thus, by the appropriate application of the analytical or numerical method the growth-rate constants  $p_{ij}$  or  $q_j$ , and the composition profile across the coating can be calculated, for any surface composition. The Al intake of the nickel specimen,  $W_s$ , and the rate constant  $K_s$  are then obtained by integrating the profile.

In Fig. 1 (a) and (b) the  $K_s$  versus surface composition curves at  $1093^\circ\text{C}$  and  $800^\circ\text{C}$  have been superimposed on the  $K_g$  curves to locate their intersections.

#### Comparison with Experiment

Data have been obtained for the aluminization of unalloyed Ni in packs activated with  $\text{AlF}_3$ ,  $\text{NaF}$ ,  $\text{NaCl}$  and  $\text{NaI}$ . The packs contained 4 w/o Al, 4 w/o activator, balance  $\text{Al}_2\text{O}_3$ , and were contained in alumina-lined iron retorts with a slide-fitting cover. The retorts were heated in an atmosphere of  $\text{H}_2$ . After removal, the coated specimens were cleaned by brushing and in an ultrasonic bath. Surface compositions were determined by microprobe analysis of the as-coated surfaces.

The square of the weight gain and surface composition vs. time curves for a number of specimens are shown in Fig. 3. It was observed that surface melting had occurred on specimens aluminized at  $1093^\circ\text{C}$  in packs

activated with  $\text{AlF}_3$  and  $\text{NaF}$ , and curves for these specimens are not given. Also low and erratic weight gains were obtained with  $\text{NaI}$  activated packs, and these results are not shown. For the remainder of the activators and temperatures studied it was observed that the surface compositions of the coated specimens were relatively independent of time. Furthermore the square of weight gain vs. time curves were nearly straight line obeying parabolic relationship. These results indicate that within a short period the system reaches steady-state at the pack coating interface. The surface compositions obtained under various conditions are compared with those predicted theoretically in Table 1. It will be noted, the activators are properly ordered by the theory. Furthermore, there is good correspondence between the predicted and observed values of surface composition. This is felt to be a strong confirmation of the basic validity of the proposed model.

#### Summary and Conclusions

By combining the gaseous diffusion model of Levine and Caves with a calculation of diffusion rates in the solid a theory of pack aluminization has been formulated. This theory relates the surface composition of the coating (and therefore, in principle, the coating formation rate) to pack operating parameters such as pack Al density, type of activator, temperature and others. Experimental data on the aluminization of unalloyed Ni in pure Al packs obtained by us to date are in good agreement with the predictions of the theory.

Acknowledgement: This work was supported in part by the NASA Lewis' Research Lab under Grant No. NGR 33-015-160.

Table 1. Comparison of theoretically predicted and observed results

Pack Conditions		Phase; Surface composition (a/o Al)	
Activator	Coating Temperature	Observed	Predicted
$\text{AlF}_3$	$1093^\circ\text{C}$	Liquid, >62.5	Liquid, >62.5
$\text{AlF}_3$	$800^\circ\text{C}$	$\text{Ni}_2\text{Al}_3$ , 59.0	$\text{Ni}_2\text{Al}_3$ , 59.10
$\text{NaF}$	$1000^\circ\text{C}$	$\text{Ni}_2\text{Al}_3$	$\text{Ni}_2\text{Al}_3$
$\text{NaCl}$	$1093^\circ\text{C}$	$\text{NiAl}$ , 53.2	$\text{NiAl}$ , 54.0

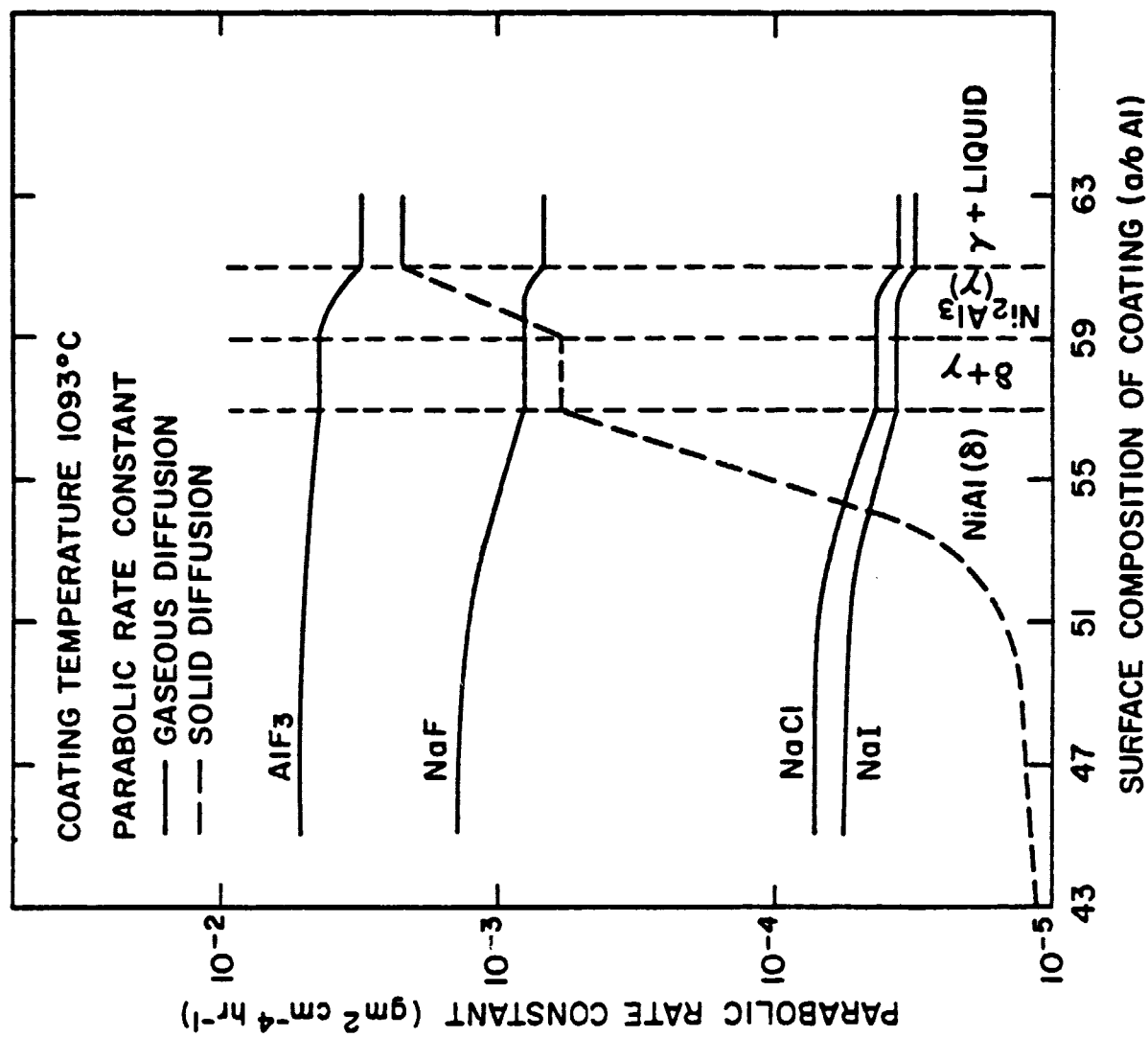
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- Fig. 1 (b) Gaseous and solid diffusion rate constants ( $K_g$  and  $K_s$ ) as a function of surface composition at  $800^{\circ}\text{C}$  (calculated).
- Fig. 2 Typical composition profiles in the diffusion zone, computed for pack aluminization at  $1100^{\circ}\text{C}$  for 20 hours.
- Fig. 3 Variation of square root weight gain and surface composition with time in pure Al packs.

Fig. 2 (a)





**RESEARCH DESIGN**

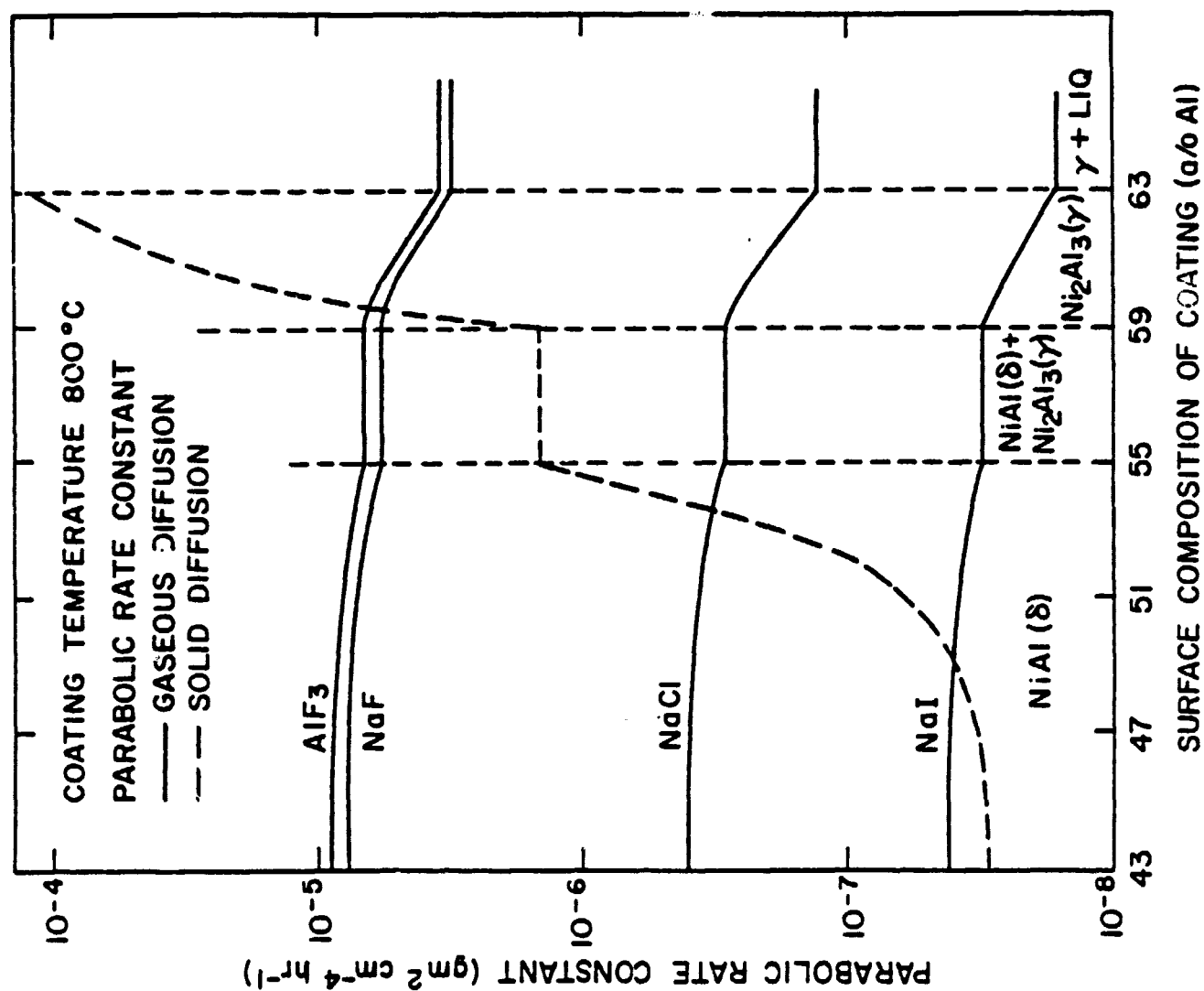


Fig. 2

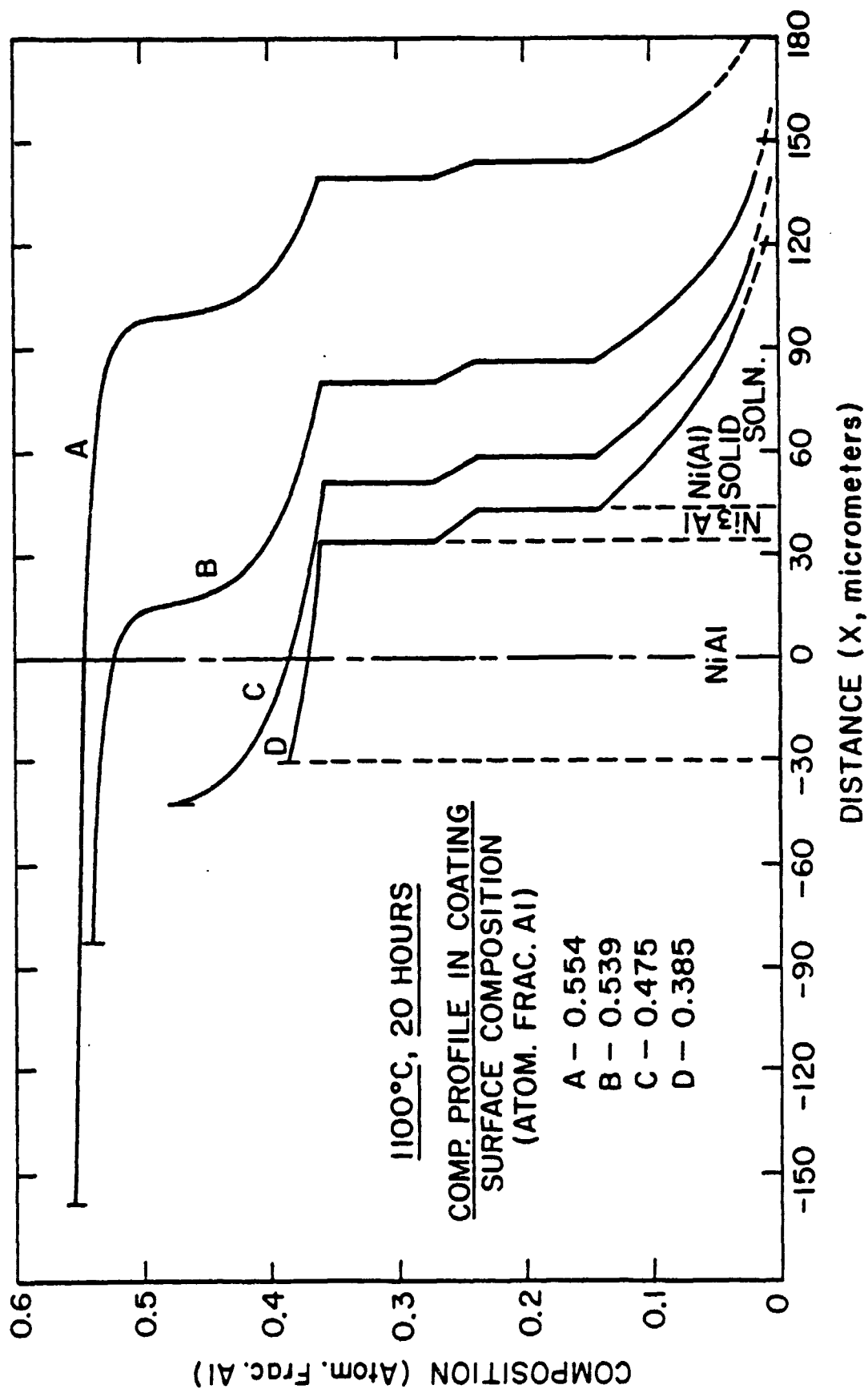


Fig. 3

