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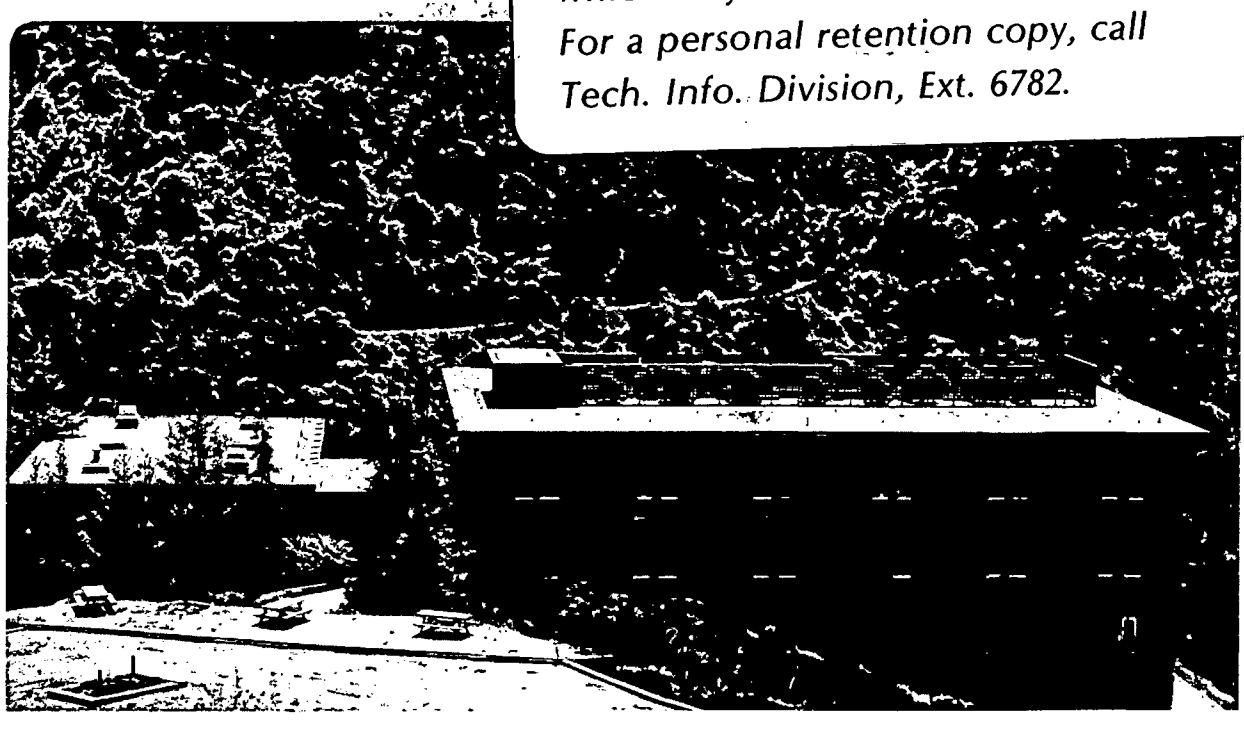

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*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U. S. Department of Energy under Contract Number DE-AC03-76SF00098.

†Deceased.

SURFACE Al COMPOSITION DURING PACK ALUMINIZING - A QUANTITATIVE MODEL - †

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ABSTRACT

The surface concentration of Al is predicted during aluminizing of pure Fe in NH_4Cl-activated pure Al pack at 1000-1400 K using a mathematical model based on the principles of thermodynamics, diffusion and phase equilibrium diagram. This model assumes that the Al depletion zone consists of a gas and liquid phase with the latter adjoining the component being coated. By invoking the continuity equations in the gaseous and liquid phases, the surface Al composition is predicted. By this model, pack aluminization can be classified as a) high surface Al concentration at low temperatures, and b) low surface Al concentration at high temperatures. This model yielded predicted surface Al concentration in agreement with experimental data.

Keywords: Aluminizing, Quantitative, Model, Fe

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INTRODUCTION

Pack aluminizing is a process in which Al is diffusionally added to a piece of material, e.g. Fe or Fe-based alloys in a halide gaseous environment generated and maintained by a system of chemical reactions involving the elemental chemical species Al, Cl, H, N in the case of NH_4Cl-activated packs. Initially, a solid mixture of pure Al or Fe-Al alloy powders, halide salt, e.g. NH_4Cl, and Al_2O_3 are tumbled together so as to obtain a thorough mixture. The pack mixture together with the material to be aluminized are placed in an iron retort or Al_2O_3 crucible with tight-fitting or semi-open covers. The entire pack content is introduced into the furnace under inert atmosphere environment. Pack aluminizing is usually done between 750-1200°C. Aluminized layers provide protection in severe corrosion environments.

The first systematic attempt to relate the effect of pack variables to coating structure was undertaken by Goward and Boone[1] and based entirely on experimental results. The surface concentration of Al after aluminizing is not identical with the pack Al concentration or as predicted by the corresponding phase equilibrium diagram, e.g. Fe-Al (Figure 2), but falls below the pack concentration by various amounts depending primarily upon the pack Al activity and type of activator used.[2,3] The structure of pure Al packs after coating reveal the presence of an Al-depleted zone in the pack next to the coated specimen.[3] The rate of Al transport in a halide activated pack as well as the rate of Al intake by the sample have been calculated by Levine and Caves[2] under the assumptions that gaseous Al halides diffuse

through an Al depleted zone in the pack adjacent to the specimen surface and that the Al activity at the coating surface is constant. Unfortunately, the concept of flux was incorrectly used in Levine's model and has persisted until now (see next section). Siegle[3] et al., using the same concept of flux as Levine's, predicted surface Al composition as a function of temperature in aluminized pure Ni by balancing the rate constants for diffusion in solid phase, K_s, with that for Al deposition, K_g. A latter model[4] considered activator depletion within the Al depletion zone in the case of condensible halides.

In the analysis of the solid state diffusional process during aluminizing, the pack content is regarded as an infinite source of activated Al (as gaseous halide) which is transported to the surface of the sample. As a consequence, the need to accurately determine the surface Al concentration and hence the boundary conditions during aluminizing is essential. More importantly, accurate characterization of the boundary conditions during aluminizing in effect assures more control when planning diffusion experiments in ternary systems employing aluminizing environments in place of the more conventional solid-solid couples.

ALUMINIZING MODEL (Pure Iron)

In the model of Levine and Caves, a σ_i factor is introduced which allows for the fact that not all of the Al carried to the surface by the gaseous specie, i, enters the specimen. In the present model, a fraction of unreacted halide gases condenses on the specimen surface

creating a thin liquid condensate superimposed on the Al-depletion zone adjoining the coated sample. As a consequence, the Al-depletion zone is maintained in part by gaseous diffusing species and an adjoining thin liquid phase condensate on the surface of the sample (Figure 1). Within the thin liquid condensate, Al is the main diffusing specie under its own concentration gradient. Using the Fe-Al phase equilibrium diagram (Figure 2), it is predicted that the halide gases condense with an effective Al concentration corresponding to that associated with the stoichiometric θ phase. Within the thin liquid condensate, there is an Al concentration gradient varying from that of stoichiometric θ phase ($FeAl_3$) to that corresponding to the effective surface Al composition on the specimen. Thus, by balancing fluxes across the gaseous phase with that across the thin liquid condensate, the effective Al concentration on the surface of the sample is predicted for each temperature.

In Figure 1, OM represents the gas diffusion distance. At the interface, O, C_0 represents the concentration of Al (assumed to be the same as the activity) in the undepleted pack from which the equilibrium partial pressures of the halide gases can be calculated. At the interface, M, C_M represents the concentration of Al at which the gases condense and corresponds to that of the stoichiometric θ phase. At the interface, S, C_S represents the effective Al concentration on the surface of the aluminized sample. The fluxes in the gas phase are summed over the three principal halide gases (AlCl, $AlCl_2$, $AlCl_3$) as described in the next section and represented as j_g while that associated with the liquid phase is represented as j_L (see Appendix 1a).

Linearization leads to the expression K with units of gm/cm-sec and which was referred to as the instantaneous flux in Levine's model. The units of flux are gm/cm^2-sec. Thus, by equating the K expressions in the liquid and gas phases, the surface Al composition C_s is predicted. In the liquid phase, the diffusivity is that of Al.

METHOD OF CALCULATING EQUILIBRIUM HALIDE PARTIAL PRESSURE

First, only the gaseous species, AlCl, $AlCl_2$, $AlCl_3$, HCl, and H_2 are assumed present in large enough quantities to influence the reaction equilibria as fixed by the NH_4Cl/Al system. On heating, NH_4Cl dissociates completely according to the reactions:

$$NH_4Cl\ (g) \rightarrow NH_3\ (g) + HCl\ (g) \qquad [1]$$

$$2NH_3\ (g) \rightarrow N_2\ (g) + 3\ H_2\ (g) \qquad [2]$$

From the magnitude of the rate constants, the reaction:

$$2Al(1) + N_2\ (g) \rightarrow 2AlN \qquad [3]$$

proceeds to completion at high temperature so that N_2 is not present in the system in sufficient amounts to influence the gaseous equilibria. The following three reaction equations are used to relate the gaseous species in equilibrium with liquid Al:

$$2HCl\ (g) + 2Al(1) \rightleftharpoons 2AlCl\ (g) + H_2\ (g) \qquad [4]$$

$$2HCl\ (g) + Al(1) \rightleftharpoons AlCl_2\ (g) + H_2\ (g) \qquad [5]$$

$$6HCl\ (g) + 2Al(1) \rightleftharpoons 2AlCl_3\ (g) + 3H_2\ (g). \qquad [6]$$

Assuming that the gases behave ideally so that the component activities are identical with component partial pressures, the equilibrium constants at T K for the three equations are respectively: (for $a_{Al} = 1.0$)

$$K_1 = \frac{P^2_{AlCl} \cdot P_{H_2}}{P^2_{HCl}} \qquad [7]$$

$$K_2 = \frac{P_{AlCl_2} \cdot P_{H_2}}{P^2_{HCl}} \qquad [8]$$

$$K_3 = \frac{P^2_{AlCl_3} \cdot P^3_{H_2}}{P^6_{HCl}} \qquad [9]$$

Let the following nomenclature be used:

x_1 = mole fraction of AlCl (g) in equilibrium gas mixture,

x_2 = mole fraction of $AlCl_2$ (g) in equilibrium gas mixture,

x_3 = mole fraction of $AlCl_3$ (g) in equilibrium gas mixture,

x_4 = mole fraction of H_2 (g) in equilibrium gas mixture,

x_5 = mole fraction of HCl (g) in equilibrium gas mixture,

x_6 = no. of moles of Al per mole of HCl (g) originally,

x_7 = no. of moles of product gases per mole of HCl.

Then a system of seven simultaneous equations may be generated from three atom balances, a mole fraction restraint and three equilibrium relations.

Atom conservation balances: The number of atoms of each element entering equals the number of atoms of each element in the equilibrium mixture.

Aluminum: $x_6 = (x_1 + x_2 + x_3)\, x_7$ [10]

Hydrogen: $4 = (2x_4 + x_5)\, x_7$ [11]

Chlorine: $1 = (x_1 + 2x_2 + 3x_3 + x_5)\, x_7$ [12]

Mole fraction restraint:

$$x_1 + x_2 + x_3 + x_4 + x_5 = 1 \qquad [13]$$

Equilibrium relations:

$$K_1 = \frac{x_4 \cdot x_1^2}{x_5^2} \qquad [14]$$

$$K_2 = \frac{x_2 \cdot x_4}{x_5^2} \qquad [15]$$

$$K_3 = \frac{x_3^2 \cdot x_4^3}{x_5^6} \qquad [16]$$

The relations [14], [15] and [16] follow directly from [7], [8] and [9] respectively, where $P_{AlCl} = x_1$, etc. and assuming the total pressure is 1. In addition, there are five side conditions:

$$0 \leq x_i \leq 1 \qquad i = 1,2, \ldots, 5 \qquad [17]$$

The above conditions insure that all mole fractions in the equilibrium mixture are non-negative; that is, any solution of equations [10] to [16] that contains negative mole fractions is physically meaningless. From physical-chemical principles, there is one and only one solution of the equations that satisfies conditions [17]. A standard computer program based on the Gauss-Seidel[5] process was used to solve the equations. In Figure 3 are shown the equilibrium partial pressures of the three principal halide species with temperature. The results compare very favorably with those of Siegle's[3] although different approaches were used in each case.

To calculate the partial pressures at which the halides condense, hydrogen and chlorine mass balance equations are used in place of equations [11] and [12] and then solved simultaneously with equations [4], [5] and [6]. Fuller et al.[6] have pointed out that the Gilliland equation for gas diffusivity should not be used because there is associated average error of 21.1%. They derived instead the following equation, which they showed to have an associated average error of only 4.3% when compared with experimental values:

$$D_{AB} = \frac{(1 \times 10^{-3})\, T^{1.75}}{P(v_B^{1/3} + v_A^{1/3})^2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}\ cm^2/sec. \qquad [18]$$

where T = temperature, P = pressure (atm); M_A, M_B are molecular weights of species A and B in gm/gm-mole; and v_A, v_B are diffusion volumes. This equation has been adopted in the present study. The medium in the present case is helium. For estimating the diffusivity of Al in the liquid, the equation of Sutherland[7] is used:

$$D_{Al} = \frac{\gamma_B T}{4\pi R \mu} \qquad [19]$$

where γ_B = Boltzmans constant, R = radius of Al, T = temperature (K), and μ = viscosity of Al liquid. In Figure 4 is shown the partial pressures of the respective halide gases at different temperatures on the surface of the thin liquid film.

Also, according to Levine's model, a σ_i factor will be introduced to the respective fluxes associated with specific halide gases via:

$$3AlCl = AlCl_3 + 2Al;\ \sigma_i = 2/3 \qquad [20]$$

$$3AlCl_2 = 2AlCl_3 + Al;\ \sigma_i = 1/3 \qquad [21]$$

Hence, from Appendix 1a:

$$\sum_{i=1}^{n} \frac{M_i D_i \sigma_i (P_i^{\circ} - P_i^{m})}{RT} = D_{Al} (C_{\theta} - C_s) \rho_{Al} \qquad [22]$$

where the factor M_i/RT is introduced to convert partial pressures P_i into concentrations (gm/cm^3).

Predicted and Experimental Surface Al Compositions

In Figure 5 are shown the values of predicted surface Al compositions after pack aluminizing pure Fe in pure Al-pack. The results of Heckel et al.[8] have shown that η phase is present on the surface between 1053 K and 1273 K after the aluminizing of Fe in a pure Al pack (NH_4Cl-activated + 35 w/o Al). The η phase has a narrow composition range (70-72 a/o Al) and this value is consistent with present theoretical predictions. The present model also predicts a transition region between > 1200 - < 1300 K where the surface Al composition becomes a strong function of temperature. The present model predicts that a pure Al pack can be regarded as a high activity pack at low temperatures and as a low activity pack at high temperatures during aluminization of pure Fe. The transition between the two regimes is abrupt. A 20 w/o Al-5 w/o NH_4Cl activated pack was used in aluminizing pure Fe at two temperatures, and the experimentally determined surface Al compositions shown in Figure 5 compare favorably

with theoretically predicted values. Also, the above theoretical predictions of surface Al content with temperature are consistent with the results of Goward and Boone[1] in nickel-base alloys.

In Figures 6 and 7 are shown the cross-sections of pure Fe after aluminizing at 1200 K and 1350 K respectively in 20 w/o Al, 5 w/o NH_4Cl pack. The surface phases correspond to η and ξ respectively.

APPENDIX 1a

FLUX EQUATIONS:

GAS	LIQUID	SOLID
$\sum_{i=1}^{3} j = j_G = -\sum_{i=1}^{3} D_i \frac{\partial C_i}{\partial X}$	$j_L = -D_i \frac{\partial C}{\partial X}$	

APPROXIMATE CONCENTRATION PROFILE IN GAS PHASE AS LINEAR. INTEGRATE FICK'S LAW AS:

$$j_G \int_0^m dX = -D \int_{C_o}^{C_m} dC$$

IF BOUNDARY CONDITIONS ARE FIXED THEN INSTANTANEOUS FLUX AT ANY THICKNESS M

$$j = 1/m \int_{C_m}^{C_o} D\,dC = K/m \qquad \text{Units of K (g/cm sec)}$$

$$K = \int_{C_m}^{C_o} D\,dC \simeq \sum_{i=1}^{3} D_i \,(P_i^{\circ} - P_i^{m})$$

SIMILARLY FOR LIQUID: $K = D(C_m - C_s)$

$j_G m = j_L (N - m) \longleftrightarrow K_G = K_L$

XBL 828-11191

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FIGURE CAPTIONS

Figure 1. Schematic sketch of depletion zone.

Figure 2. Fe–Al phase equilibrium diagram.

Figure 3. Calculated equilibrium halide gases with temperature in the undepleted pack.

Figure 4. Calculated equilibrium halide gases with temperature at condensation interface.

Figure 5. Predicted and experimentally determined surface Al composition for aluminized pure Fe with temperature.

Figure 6. Cross section through pure Fe after aluminizing in 20 w/o pure Al–NH_4Cl pack at 1200 K.

Figure 7. Cross-section through pure Fe after aluminizing in 20 w/o pure Al–NH_4Cl pack at 1350°K.

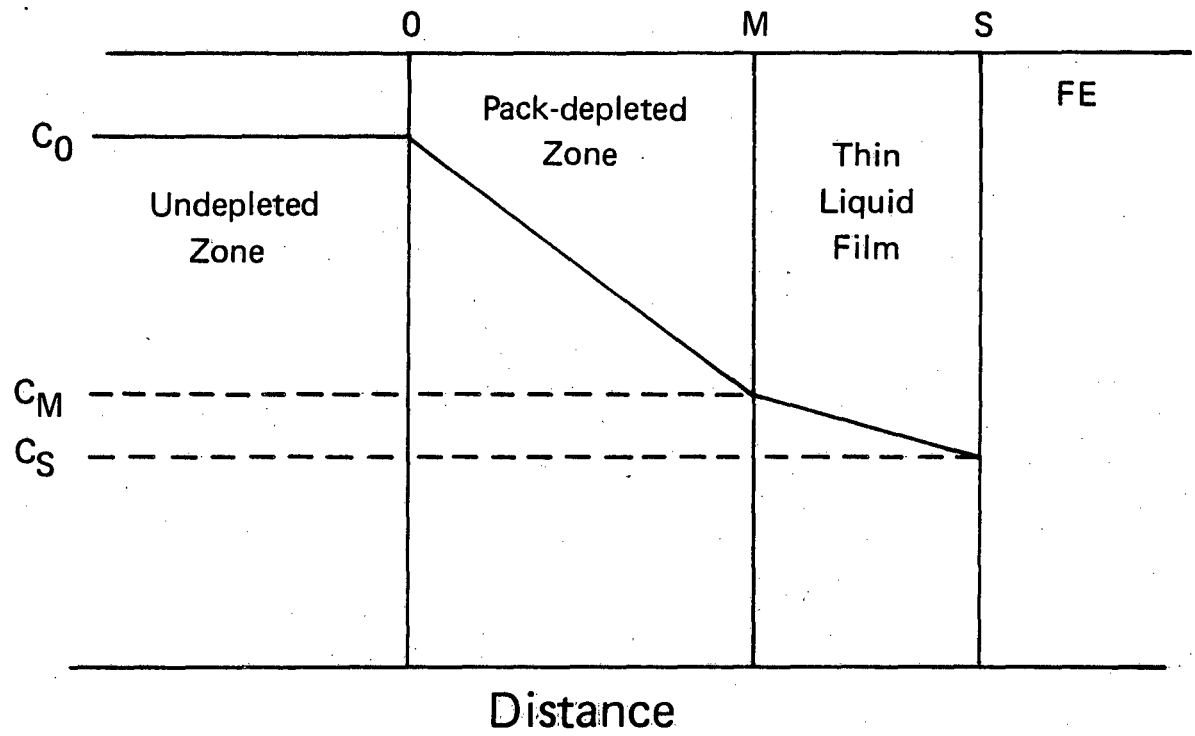

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Fig. 1

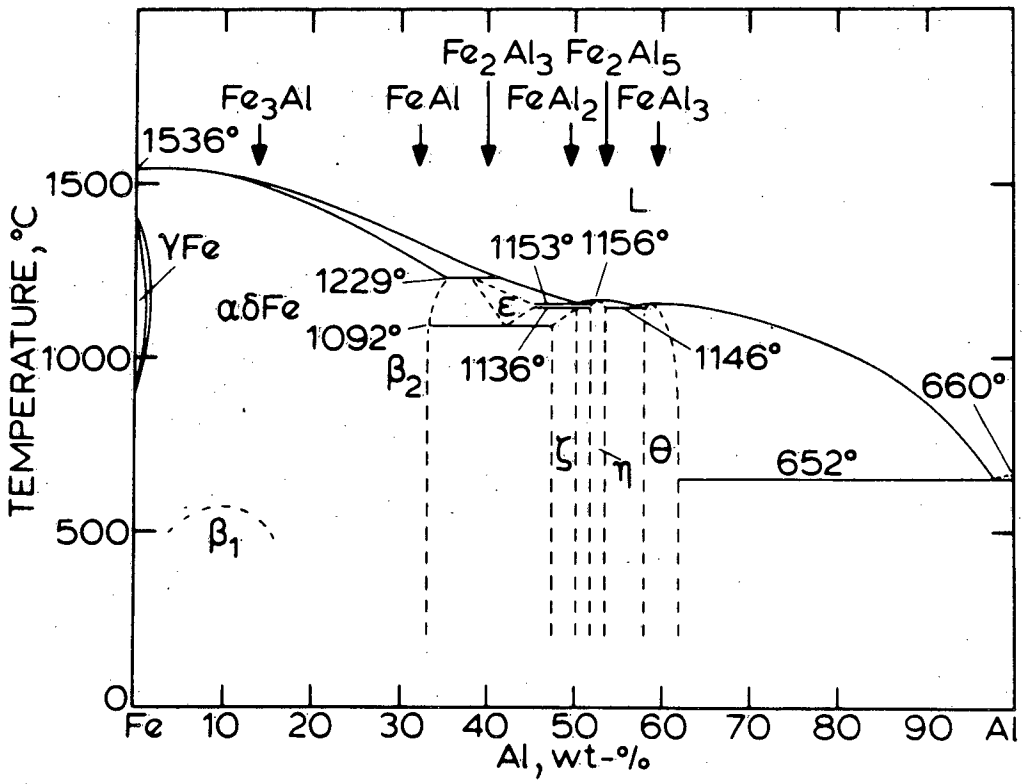

Fig. 2

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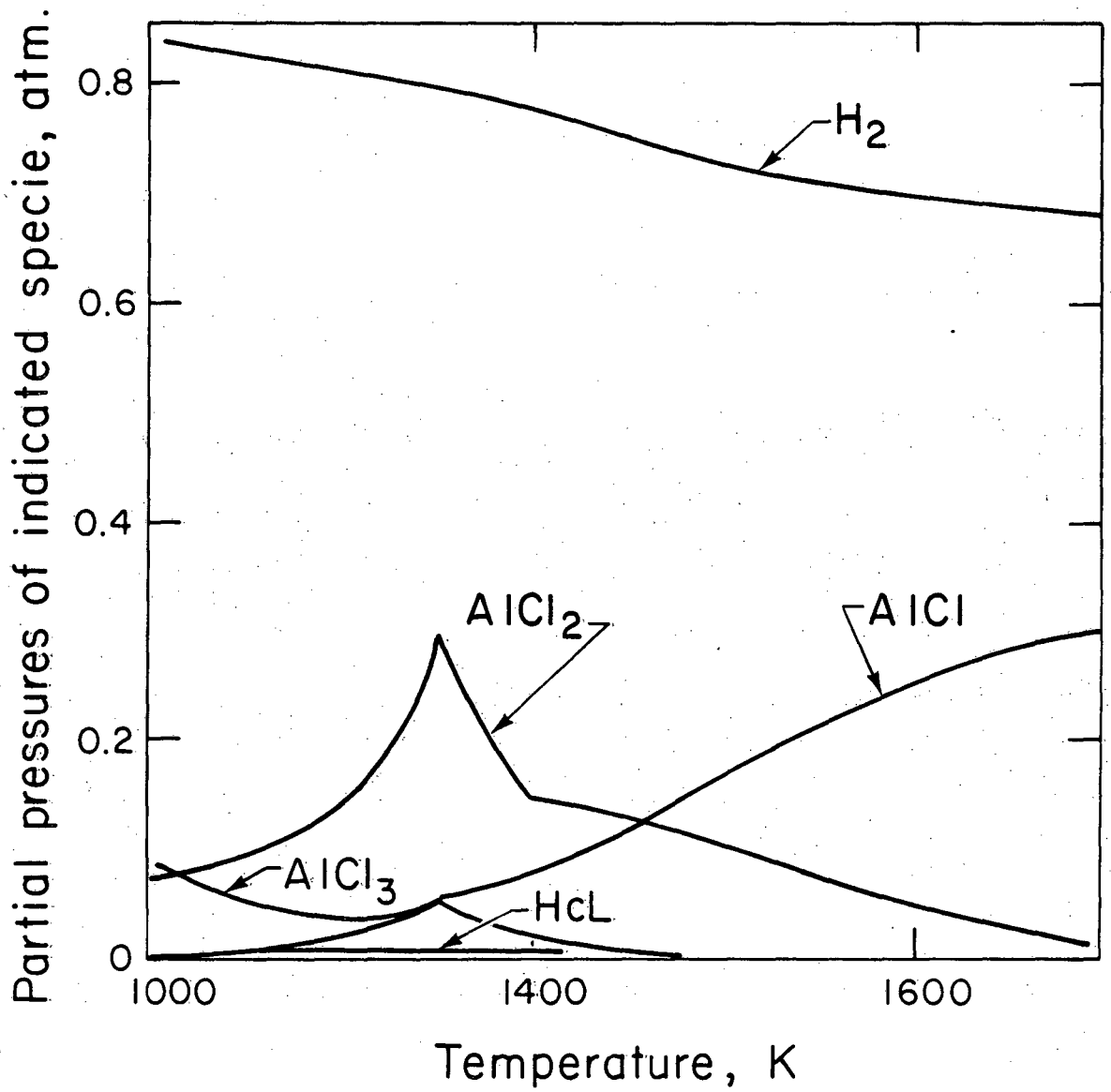

Fig. 3

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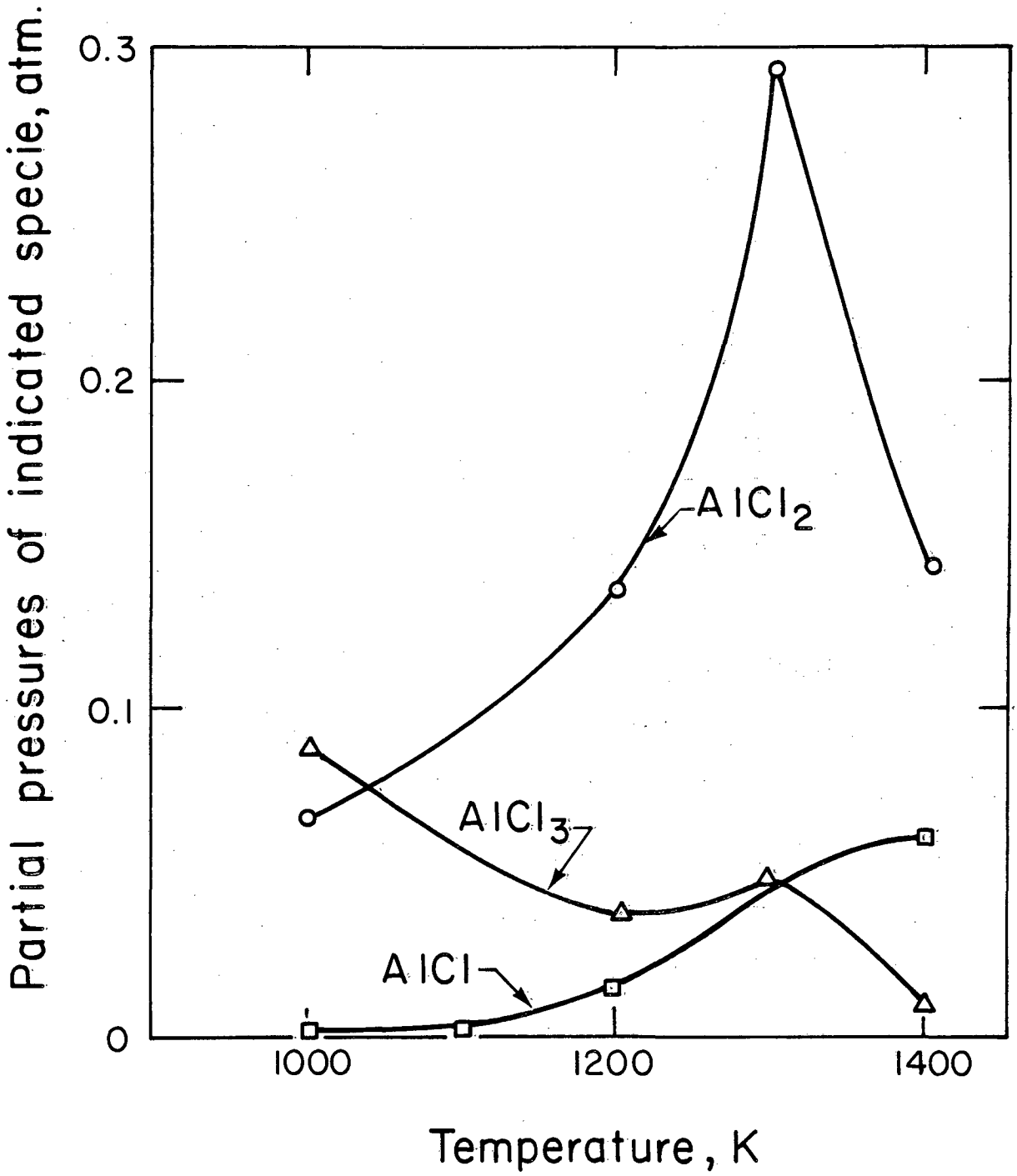

Fig. 4

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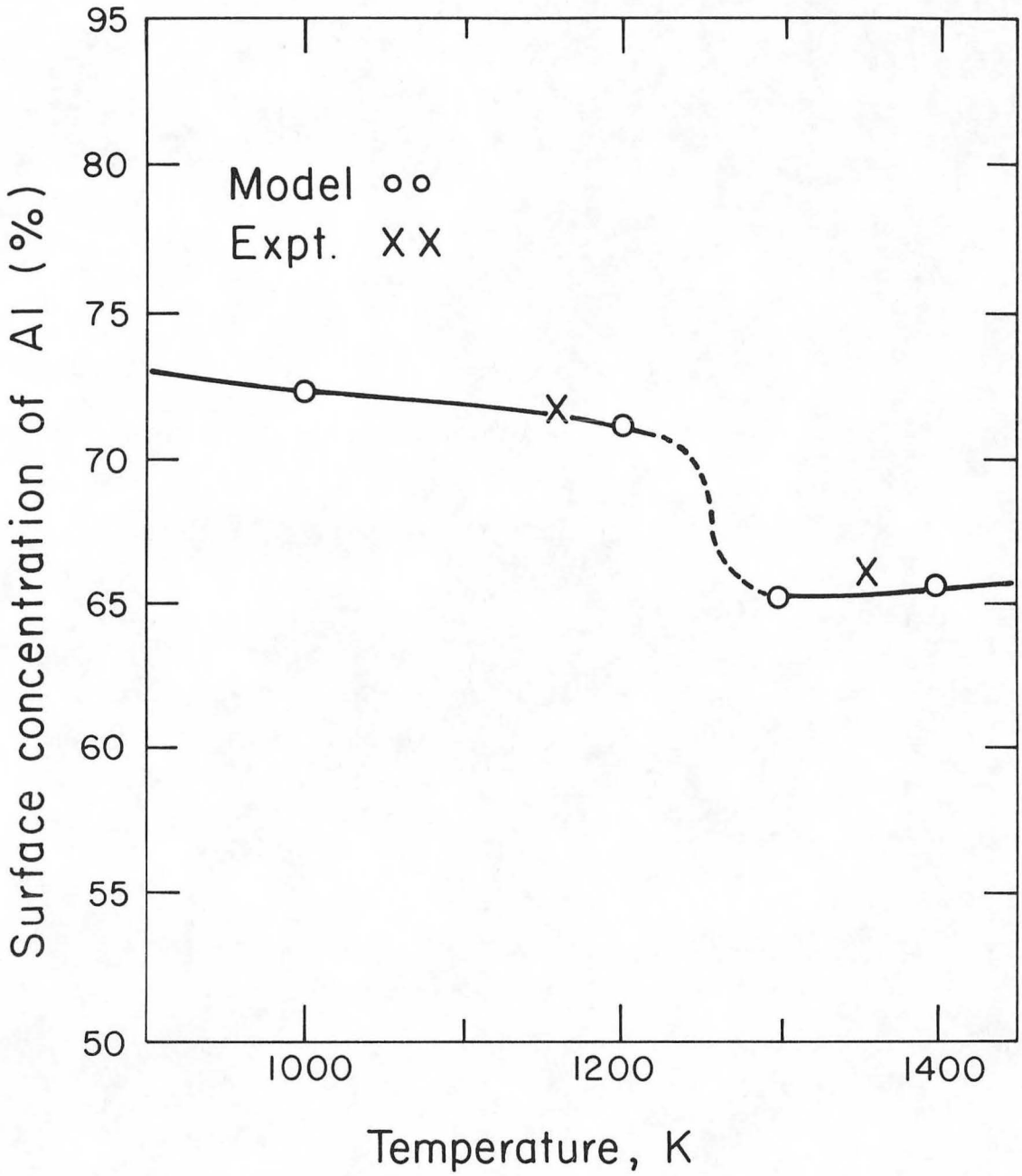

Fig. 5

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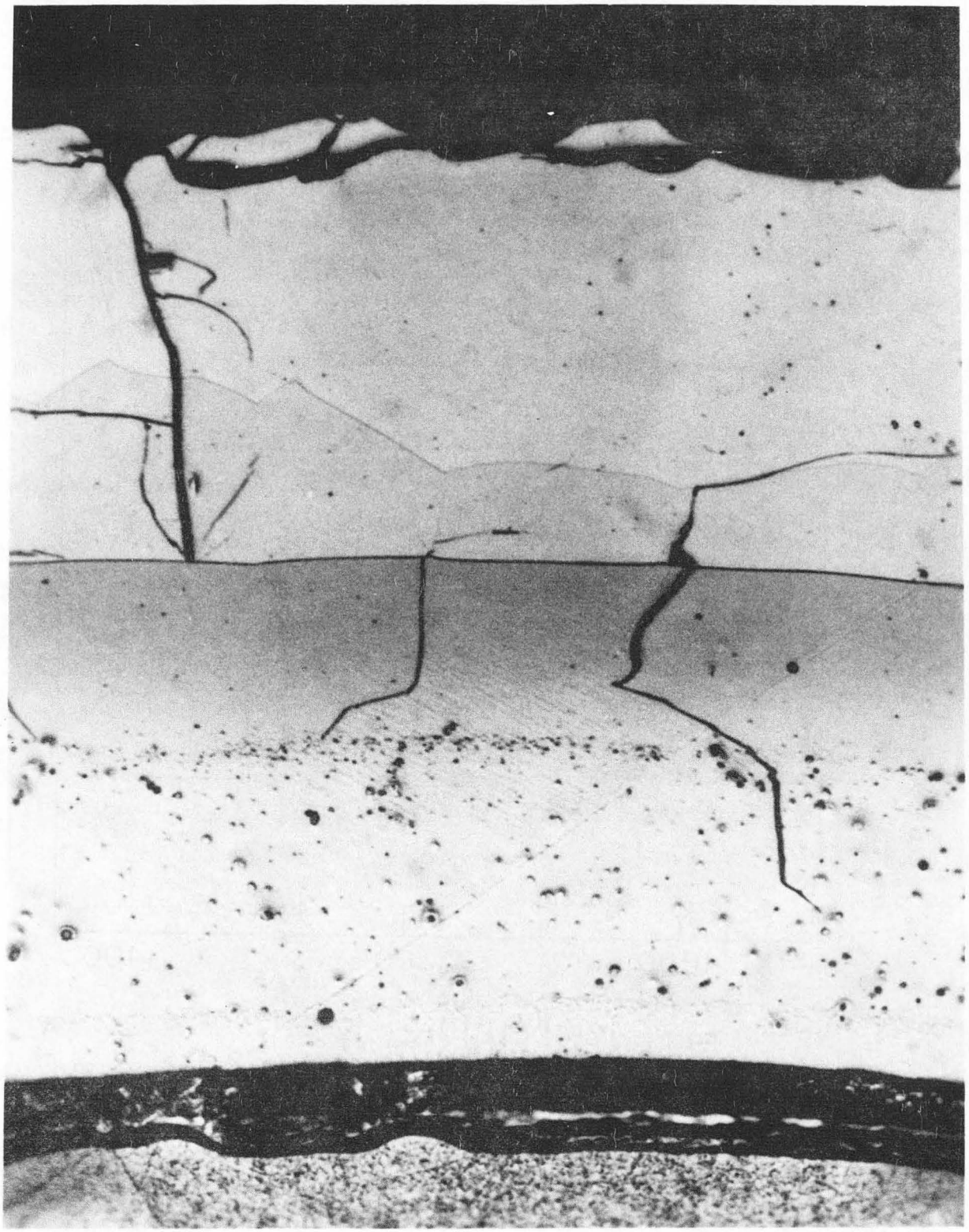

Fig. 6

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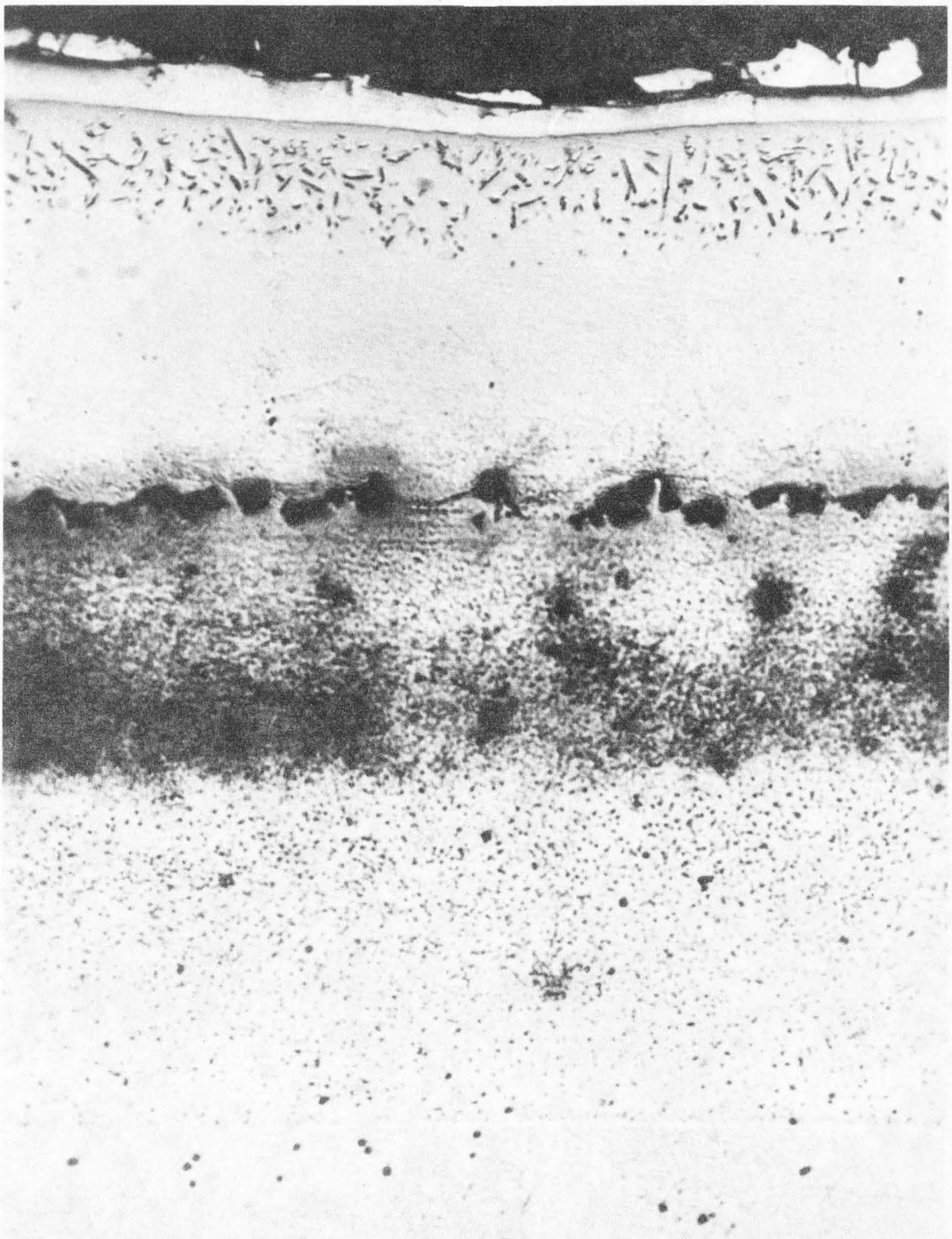

Fig. 7

XBB 820-9072

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