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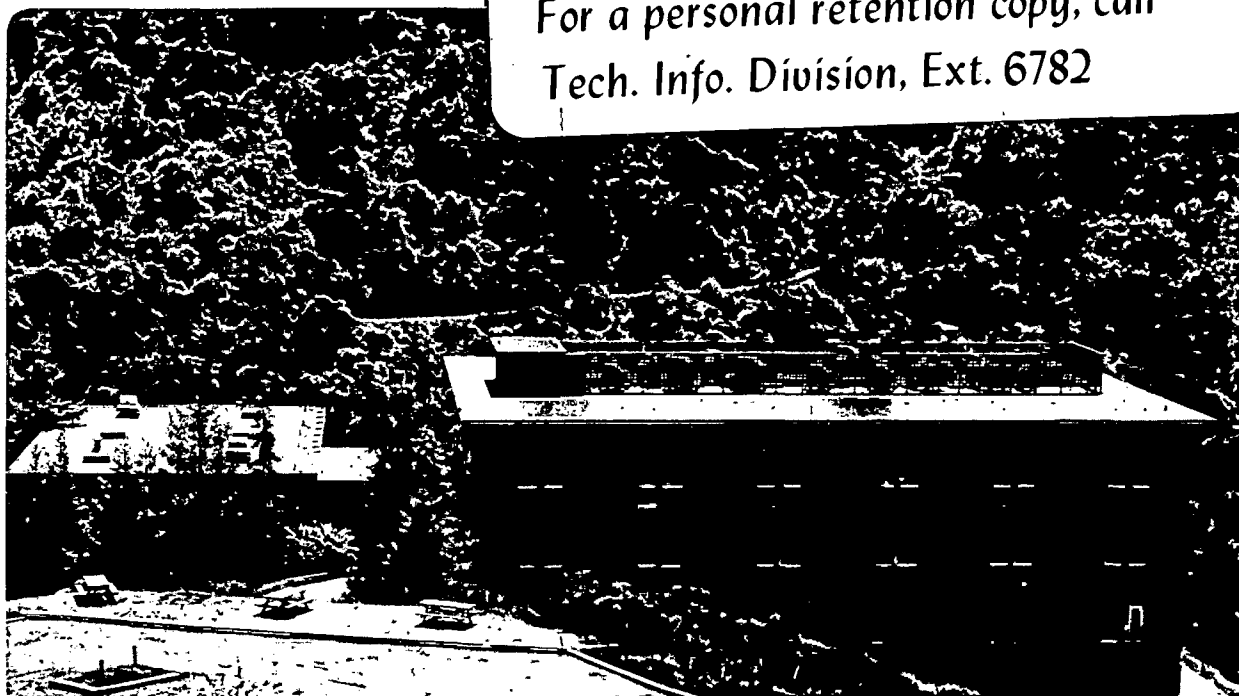
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INTERDIFFUSION IN THE Fe-Al SYSTEM: ALUMINIZING

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ABSTRACT

Interdiffusion coefficients in the Fe-Al system have been measured up to Al concentrations of 50 at.%. An aluminizing pack was used as the source of Al, and consisted of a powder mixture of Al_2O_3 , Fe-50% Al and an activator. The temperature and composition dependence of the diffusion coefficients were evaluated and compared with predictions of existing models for alloys of high solute content.

Keywords: Aluminizing, Fe-Al, Diffusion.

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I. INTRODUCTION

Aluminizing of Fe-base alloys has received revived impetus of late as a means of improving the high temperature corrosion resistance of materials likely to be considered in many energy related applications. If the surface of the component is enriched in Al, this ensures the formation of an Al_2O_3 scale on subsequent exposure to high temperature oxidizing environments, nominally without affecting the mechanical properties of the substrate. Al_2O_3 is exceptional as a protective oxide. It thickens very slowly due to its low intrinsic defect concentration, and is chemically very stable. In addition, the relatively well developed methods of promoting keying of the oxide scale to the substrate are amenable to Al_2O_3 -forming materials, and this adequately takes care of problems associated with poor scale-metal adherence.

There are a number of processes available for enriching the surface of a material with Al, such as metal spraying, electrodeposition, vapor deposition, pack cementation, etc. Although not all such processes involve elevated temperatures during the deposition process itself, during subsequent service, interdiffusion between the surface layers and substrate takes place and this has two deleterious effects. Firstly, the ability of the alloy surface to maintain the protective Al_2O_3 scale is diminished, and secondly, the mechanical properties of the substrate may well be impaired by the influx of Al from the coating, or from the loss of strengthening components from the substrate.

As a consequence, in order to predict and control the deposition process itself, as well as the subsequent degradation, there is a need for values of the interdiffusion coefficients in these Al-containing systems. Previous studies (1-4) have shown a strong dependence of the interdiffusion coefficient on composition in binary Fe-Al alloys and this study has been undertaken to examine this, and provide a basis for later studies of diffusion in multi-component Fe-base systems containing Al. The overall aim of the latter part is an attempt to minimize the degradation of Al-rich surface coatings by interdiffusion with the substrate. Attempts to suppress this effect by the interposition of a physical diffusion barrier have up to now proved largely unsuccessful. However, it must be remembered that the criterion for the development of a protective Al_2O_3 surface scale requires a sufficiently high

surface concentration of Al, whilst interdiffusion with the substrate is dependent on the Al activity gradient. Thus, if the activity gradient could be reduced, but the composition gradient retained, then the conflicting requirements could perhaps be satisfied, and the rate of degradation of the coating minimized.

II. ALUMINIZING PROCESS

Aluminizing is probably the most economical way of enriching the surface with Al. It is also the most convenient way of producing well characterized concentration profiles of Al and hence measuring the interdiffusion coefficient. It is a pack cementation process. The component or sample to be aluminized is embedded in a pack comprising of a solid mixture of pure Al or Fe-Al alloy powders, Al_2O_3 as an anti-sintering agent and a halide salt, e.g. NH_4Cl , as activator. The activator is used to generate an aluminum halide vapor phase within the pack which effectively transports the Al to the surface of the component to be coated. The pack mixture is placed in an iron or Al_2O_3 retort with tight-fitting cover, and heated to the aluminizing temperature, usually under H_2 or an inert gas.

The effective concentration of Al at the surface during aluminizing has been found to remain constant with time (2,5). However, this often corresponds to an Al activity somewhat lower than that prevailing in the pack and this is usually attributed to the aluminizing process being dependent both on gaseous transport within the pack, and solid state diffusion in the component. The difference between the Al activity in the pack and that at the sample surface depends upon the composition of the pack and the type and concentration of activator (5-8). In the present work, it suffices to note that it is time-invariant, and thus in analyzing the diffusional processes in the alloy, the pack can be regarded as an infinite source of Al.

According to the Fe-Al phase diagram, the most recent of which is shown in Figure 1 (9-11) the intermediate phases that can form during aluminizing depend on the Al activity in the pack and hence at the surface. Short of pure Al being deposited ($a_{\text{Al}} = 1$) the next intermediate phase that can form is the θ -phase ($T < 1150^\circ\text{C}$). Diffusional processes coupled with equilibrium phase relations require that phases lower in Al be present in regions away from the surface. This implies that if θ -phase forms at the surface, then expect η , ζ , β_2 and $\alpha\delta\text{Fe}$ to form sequentially in this order at increasing distances below the surface. In the present work, using a Fe-50 wt.% Al pack,

only the ζ , β_2 and $\alpha\delta\text{Fe}$ phases are expected.

III. EXPERIMENTAL PROCEDURE

Pure iron samples measuring 8 x 8 x 2 mm were cut and their surfaces polished to a 600 grit finish. The purity of the Fe is given in Table I. The powders used to make the pack mixture were a commercial Fe-50 wt.% Al alloy powder (300 mesh), NH_4Cl and Al_2O_3 (300 mesh). These were blended in a rotating mixer overnight. A cylindrical, recrystallized Al_2O_3 crucible with specially fitting cover was used as the pack container. Aluminizing was carried out in a single zone, Lindeberg furnace which was able to control the temperature within $\pm 1^\circ\text{C}$. Temperatures of 750, 850, 950 and 1050°C were used, with times varying up to 15h. A flowing argon (grade A) environment was used in the furnace during aluminizing.

Mass change vs. time curves were obtained by weighing samples before and after the aluminizing treatment on a standard analytical balance. The samples were lightly brushed after aluminizing to remove any loosely adherent pack mixture. Samples were sectioned, metallographically prepared and the Fe and Al profiles within the aluminized layer determined by electron probe microanalysis. Standard correction procedures were used to convert the measured intensities into concentrations. In addition, samples were etched and the thicknesses of the various phase layers were measured in the optical microscope. A suitable etching agent to reveal the coating structure was particularly difficult to find: eventually, a mixture of equal parts by volume of conc. HNO_3 , H_2SO_4 and H_3PO_4 , the whole diluted with an equal volume of water, was used.

In order to extend the range of alloy compositions over which the diffusion coefficient could be measured, and as a check on the aluminizing experiments, a number of diffusion couples between Fe and Fe-20 and Fe-40 Al were constructed. The two halves of the couple were spot welded together in an evacuated chamber: insignificant diffusion would occur during the welding operation.

IV. ALUMINIZING KINETICS

Figure 2 shows the $(\text{mass gain})^2$ as a function of time for Fe aluminized at 850, 950 and 1050°C ; the mass change at 750°C was rather small. A conventional parabolic rate law is followed at all three temperatures indicating diffusion-controlled growth as expected, which is also consistent with the

surface concentration remaining constant with time. Measured parabolic rate constants were 3.1×10^{-10} , 2.0×10^{-8} and $3.0 \times 10^{-7} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ at 850, 950 and 1050°C respectively. These three values correspond to an apparent activation energy of 105 kcal/mole.

V. COATING STRUCTURE

Figure 3 shows a typical cross-section through an aluminized sample after aluminizing for 10h at 850°C. Four layers are evident in the micrograph. With the help of the phase diagram (Fig. 1) these may be identified as: an outer layer of the $\beta_2(\text{FeAl})$ phase, the largest intermediate layer of $\alpha\delta\text{Fe}$; a thin layer beneath this which is presumably the $\beta_1\text{-Fe}_3\text{Al}$ phase, and finally the original substrate, again $\alpha\delta\text{Fe}$. According to the concentration profiles presented later, the Al concentration is a smooth function of distance throughout the aluminized layer, indicating that diffusion occurred in essentially a single phase material at the aluminizing temperature. The β_2 -phase at the surface is essentially an ordered phase with a composition similar to the $\alpha\delta\text{Fe}$ matrix. The $\beta_1\text{-Fe}_3\text{Al}$ phase, again an ordered compound, presumably formed on cooling.

Figure 4 shows a similar section through an aluminized layer, although in this instance part of the pack material has been incorporated into the outer coating layer. The darker-colored particle is an Al_2O_3 inclusion from the pack. After aluminizing in a pack mixture and prior to brushing, the surface appearance of the sample is shown in Figure 5 and the particles seen adhering to the surface consists of Fe-50 Al alloy particles, condensed halide salt, and Al_2O_3 particles. In Figure 6 is shown a cross-section through an aluminized layer (un-etched) and reveals the Fe-50 Al alloy particle adhering to the surface. The central dark portion in Figure 6 is ζ phase and the lighter portions, diffusionally welded onto the aluminized surface, is the Fe_3Al single phase. The above deserves attention in view of the fact that according to Siegles model (6), NH_4Cl -activated pack should not form condensed phases.

Finally, Figure 7 shows the interface between the Fe/Fe-40 % Al diffusion couple. The original structure of the lower (Fe-40 Al) half of the couple consists of β_2 (dark) and ζ (light) phases. Loss of the ζ -phase by diffusion into the Fe-half of the couple results in the development of considerable porosity.

VI. ALUMINUM CONCENTRATION PROFILES

Figure 8 show typical Al concentration profiles after aluminizing at 950°C for various times. The profiles are plotted as functions of the parameter $x/t^{1/2}$ and can be represented by a single curve indicating diffusion-controlled growth of the aluminide layers. Perhaps more importantly the surface concentration is approximately independent of time, although it does depend on temperature. Values at the different temperatures are given in Table II. Other workers (1, 2, 5) have also found that the effective concentration of Al at the surface during aluminizing remains constant with time, and thus it is appropriate to analyze the solid state diffusion of Al into the sample as emanating from an infinite source of Al (as gaseous halide) which is transported to the surface of the sample. The surface Al concentration at the sample surface is usually, however, some 12-14% lower than that predicted from the thermodynamic aluminum activity in the pack (1, 2, 5). This is generally considered to be due to a depletion of Al (2, 7), or activator (2) in a zone of the pack next to the sample. As a consequence, the overall kinetics of aluminizing are in part determined by gaseous diffusion within the pack itself, although this does not affect the analysis of the concentration profiles and the determination of the interdiffusion coefficient in the aluminized Fe.

Similar concentrations of Figure 8 are obtained at other temperatures.

VII. ANALYSIS OF THE CONCENTRATION PROFILES

The measured concentration profiles are analyzed according to the equation given by Wagner (12), which in terms of the present system is given as

$$D(N_{Al}^*) = \frac{N_{Al}^S V_m (N_{Al}^*)}{2t(\partial N_{Al}/\partial x)_{x=x^*}} \left[(1-Y^*) \int_{-\infty}^{x^*} \frac{Y}{V_m} dx + Y^* \int_{x^*}^0 \frac{1-Y}{V_m} dx \right] \quad [1]$$

where N_{Al}^S and N_{Al}^* are the mole fractions of Al at the surface and at $x = x^*$ respectively, $Y = N_{Al}/N_{Al}^S$, V_m is the molar volume, which can be a function of composition, t is time, and x is a position coordinate measured in any convenient reference frame (in this case the surface). Equation [1] is best evaluated numerically providing the functions Y/V_m , $(1-Y)/V_m$ and $\partial N_{Al}/\partial x$ can be approximated by continuous functions. Generally, ordinary polynomials are not adequate for this purpose, because of the large errors associated with higher order polynomials. The recently developed spline function

provides a much improved function for interpolation, and it is also continuous, with continuous derivatives. In the present work, a cubic spline function has been used as the approximating function. The cubic spline is a piece-wise cubic function that interpolates the experimental function values exactly at their base points, whereby each cubic piece $P_i(x)$ of spline $g_3(x)$ is represented (9) as:

$$P_i = C_{1,i} + C_{2,i}(x-x_i) + C_{3,i}(x-x_i)^2 + C_{4,i}(x-x_i)^3.$$

The coefficients $C_{j,i}$ are determined subject to the conditions that $P_i(x)$ interpolates the function Y/V_m , $(1-Y)/V_m$, $\partial N_{Al}/\partial x$ at x_i , x_i , x_{i+1} , x_{i+1} and $P_{i-1}''(x_i) = P_i''(x_i)$, $i=2,N$. This leads to $N-1$ linear equations in the $N+1$ unknowns - the derivatives at the function values. In the case of $\partial N_{Al}/\partial x$, $(\partial N_{Al}/\partial x)_{x=0}$ and $(\partial N_{Al}/\partial x)_{x_{max}}$ can be fixed, to arrive at a strictly row diagonally dominant coefficient matrix which is invertible and has a unique solution. The error, E , associated with cubic spline interpolation is $E(h^4)$, which, since the microanalysis points are 2 μm apart, is negligible. The error associated with fitting a cubic spline over the data points is $E(h/2)^4$, which is again negligible. Subroutines for spline interpolation were available in the computer library.

VIII. INTERDIFFUSION COEFFICIENTS

Figure 9 shows the interdiffusion coefficients calculated as a function of composition from the experimentally measured concentration profiles for the four temperatures studied. $\tilde{D}$ varies by about an order of magnitude over the composition range 0-50 at.% Al. Also shown in Figure 9 as an inset, are data of other workers (1, 3, 4). In addition, Sharma's (2) and Nishida's (1) data have been plotted alongside those of the present work to aid comparison. The values of $\tilde{D}$ in the present work are averaged over values calculated from a number of measured concentration profiles obtained from samples aluminized for different times at any one temperature. The novelty of using a spline function representation of the profiles, minimizes the error associated with the determination of the gradient terms in eqn.(1), and thus most of the likely errors in the $\tilde{D}$ values stem from the errors inherent in the microprobe analysis. Generally, $\tilde{D}$'s calculated from different concentration profiles were within $\pm 5\%$.

IX. TEMPERATURE DEPENDENCE OF THE INTERDIFFUSION COEFFICIENTS

In order to calculate the activation energy for the interdiffusion process, the $\bar{D}$ versus concentration functions at each temperature were represented by their appropriate spline functions and $\bar{D}$ values at each 0.5 at.% Al obtained for each temperature. This relatively small concentration interval was chosen in order to minimize the error. Then, a least squares fit to the anticipated linear function of $\log \bar{D}$ against $1/T(K)$ enabled the activation energy, $\bar{Q}$, to be found as a function of composition. Figure 10 shows typical $\log \bar{D}$ vs. $1/T$ plots corresponding to composition ranges of excellent linear fit (5-35 wt.% Al) and ranges where there were slight deviations (35-49 wt.% Al). The least squares lines joining the experimental points are subject to the constraint that the absolute error is zero and all points are equally weighted.

Figure 11 summarizes the variation of activation energy with composition and compares the values with those obtained by other workers (inset). The activation energy decreases to a minimum at about 22.6 at. % Al and attains local maxima at about 31 and 38 at. % Al respectively. Two other minima occur at about 35 and 43 at. % Al. These data are consistent with those of Hirano et. al.(4) upto a composition of about 35 at.% Al although their absolute values are somewhat lower than those obtained in the present work. Some of the discrepancy is presumably related to approximation errors in Hirano's method of analysis.

X. RELATIONSHIP BETWEEN $\bar{D}_0$ AND $\bar{Q}$

Figures 9 and 11 have shown that both the interdiffusion coefficient and the apparent activation energy for diffusion are strong functions of composition. In self-diffusion and impurity diffusion studies, this is often rationalized in terms of the Zener's correlation (12) between enthalpy and entropy of diffusion (12-14). Thus, it is argued (12-14) that the ratio $\Delta G_T / T_S$ should be constant for all compositions, where ΔG_T is the free energy for S diffusion at the solidus temperature, T_S . This means^S that

$$\bar{D}_0 = \bar{D}(T_S) \exp (\bar{Q}/RT_S)$$

where $\bar{D}(T_S)$ is the interdiffusion coefficient at the solidus temperature and is expected to be virtually constant for all alloys.

Figure 12 shows $\ln \bar{D}_0$ as a function of $\bar{Q}/T_S$. Data points corresponding to the composition intervals 0-31 at.% Al and 43-49 at. % Al fall within a shaded scatterband which has a slope of approximately $1/R = 0.56$ as demanded

by the Zener correlation. However, data for the concentration range approximately 35-43 atomic % Al show an essentially constant value for $\ln \hat{D}_0$. Indeed, the gradient of $\ln \hat{D}_0$ versus $\hat{Q}/T_s$ is ~ 0.018 . The reason for this anomalous behavior is not immediately evident.

XI. ACKNOWLEDGEMENTS

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TABLE I - ANALYSIS OF PURE IRON SAMPLES

Element	Al(3)	As(6)	C(5)	Cr(3)	Co(3)	Cu(3)	H ₂ (2)	Pb(6)	
Analysis, ppm	20	<3	30	20	70	40	100	<10	
Element	Mu(3)	Hg(6)	Mo(3)	Ni(4)	N ₂ (2)	O ₂ (2)	P(4)	Si(3)	Na(3)
Analysis, ppm	20	<5	70	300	40	1500	20	30	20
Element	S(5)	Su(3)	W(3)	V(3)					
Analysis, ppm	40	20	10	<30					

Test Materials: (1) MPIF Standard 2-43; (2) Vacuum Fusion;
 (3) Spectrograph; (4) ASTM Analytical Materials;
 (5) Combustion; (6) Food Chemicals Codex.

TABLE II - SURFACE COMPOSITIONS AFTER ALUMINIZING

<u>Temperature, °C</u>	<u>Al Conc., Atomic %</u>
750	55.0
850	54.4
950	55.5
1050	50.0

FIGURE CAPTIONS

- Figure 1. The Fe-Al phase diagram (9-11).
- Figure 2. Aluminizing kinetics for pure iron at 850-1050°C.
- Figure 3. Typical cross-section through Fe aluminized for 10h at 850°C.
- Figure 4. Cross-section through Fe aluminized for 10h at 850°C showing the incorporation of Al_2O_3 particles from the pack into the coating.
- Figure 5. Surface of Fe sample after aluminizing.
- Figure 6. Section through particle of pack (Fe-50 Al) adhering to surface.
- Figure 7. Interface of diffusion couple between Fe and Fe-40 Al after diffusion.
- Figure 8. Typical Al concentration through Fe aluminized at 950°C.
- Figure 9. Fe-Al interdiffusion coefficient as a function of temperature.
- Figure 10. $\log \bar{D}$ as a function of reciprocal temperature for four different compositions.
- Figure 11. Apparent activation energy for interdiffusion in Fe-Al system as a function of composition.
- Figure 12. $\ln \bar{D}_0$ as a function of Q/T_s for the Fe-Al system.

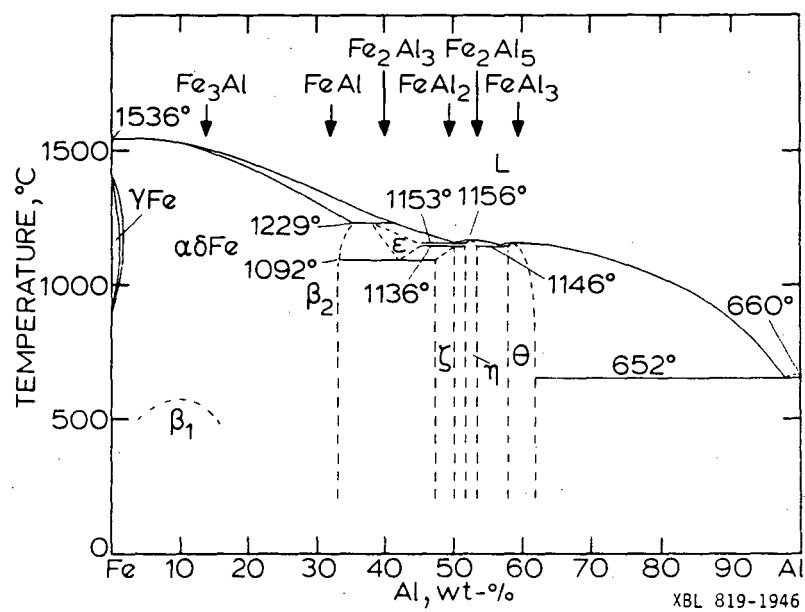
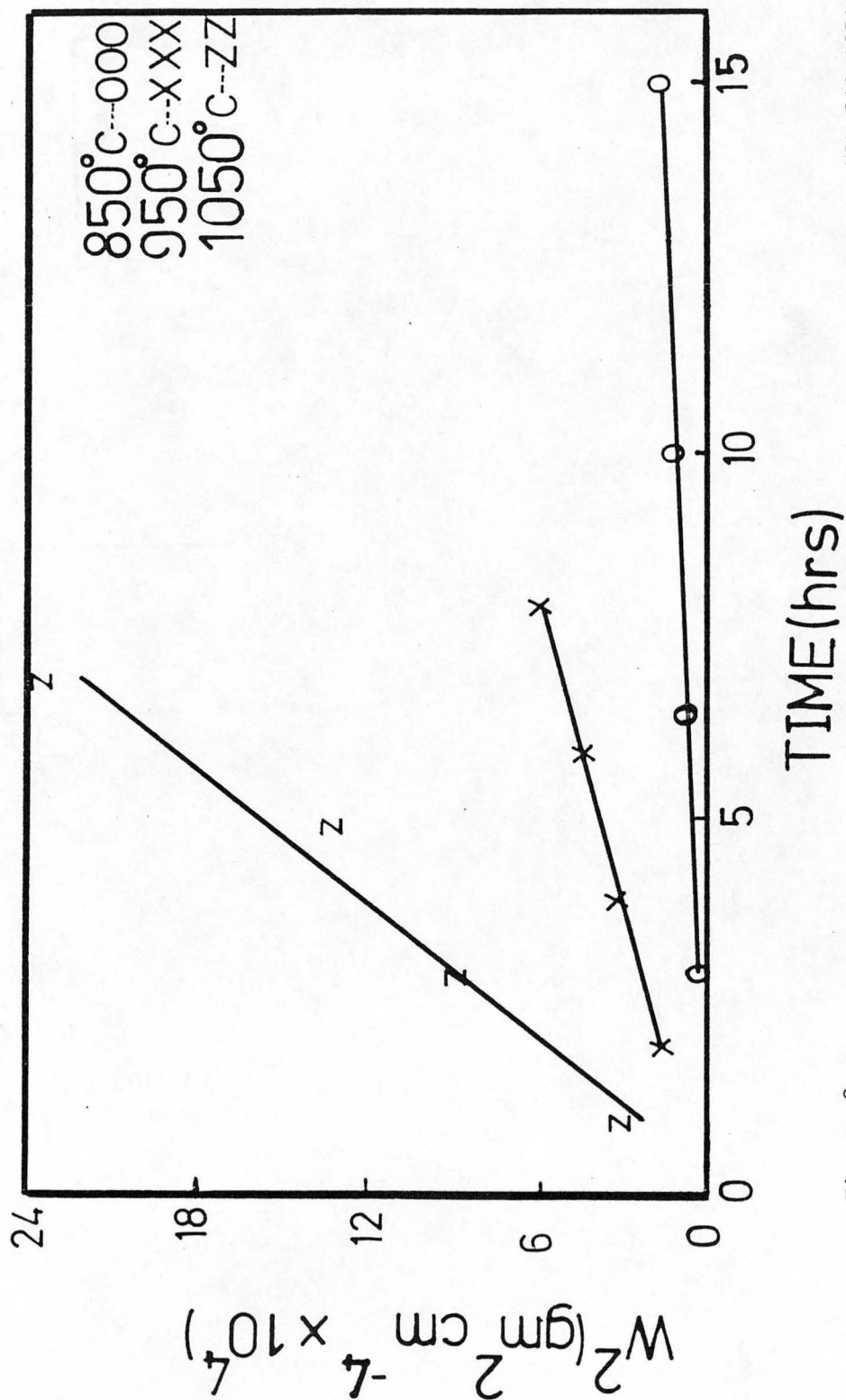


Figure 1.



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Figure 2.

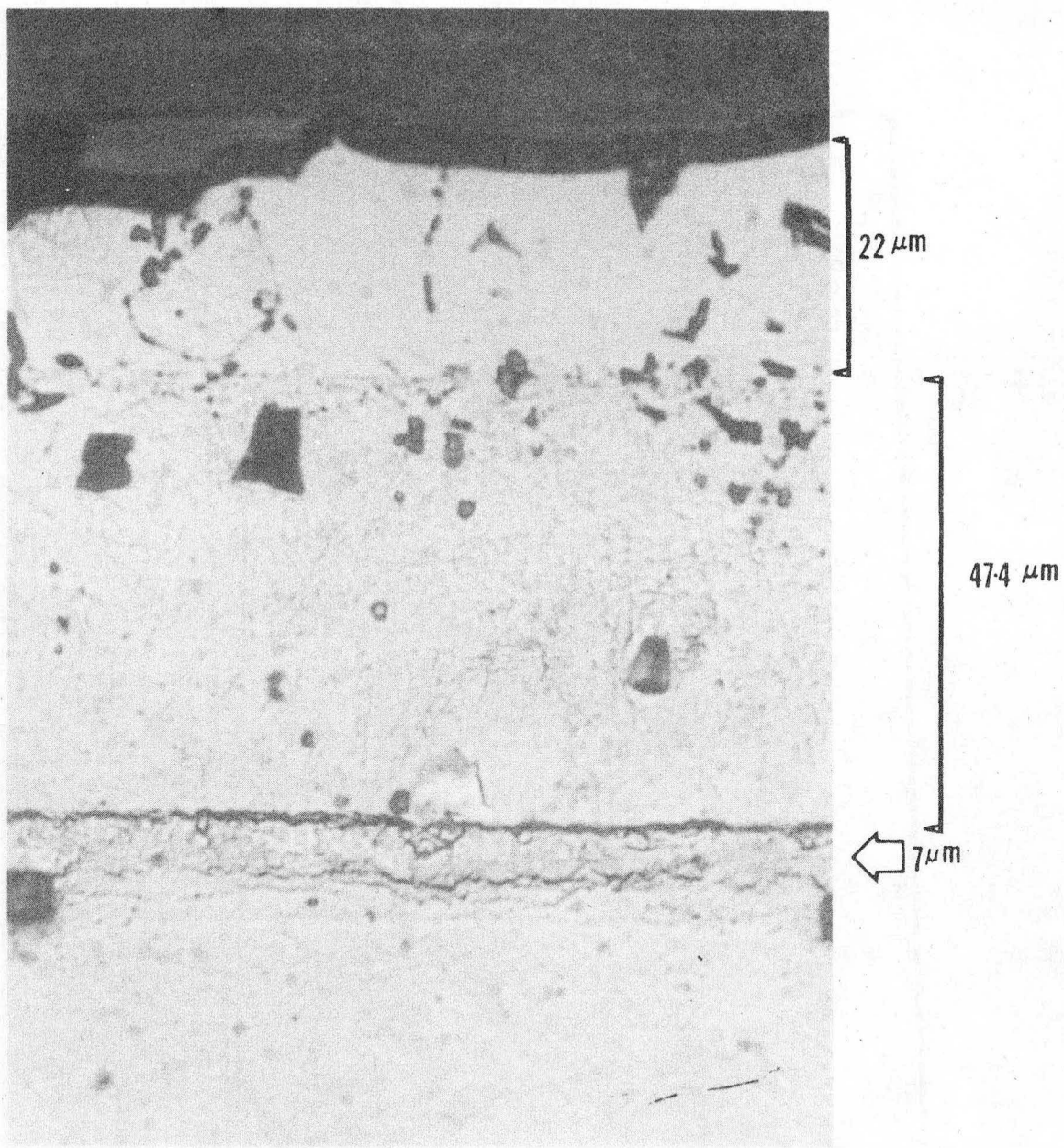


Figure 3

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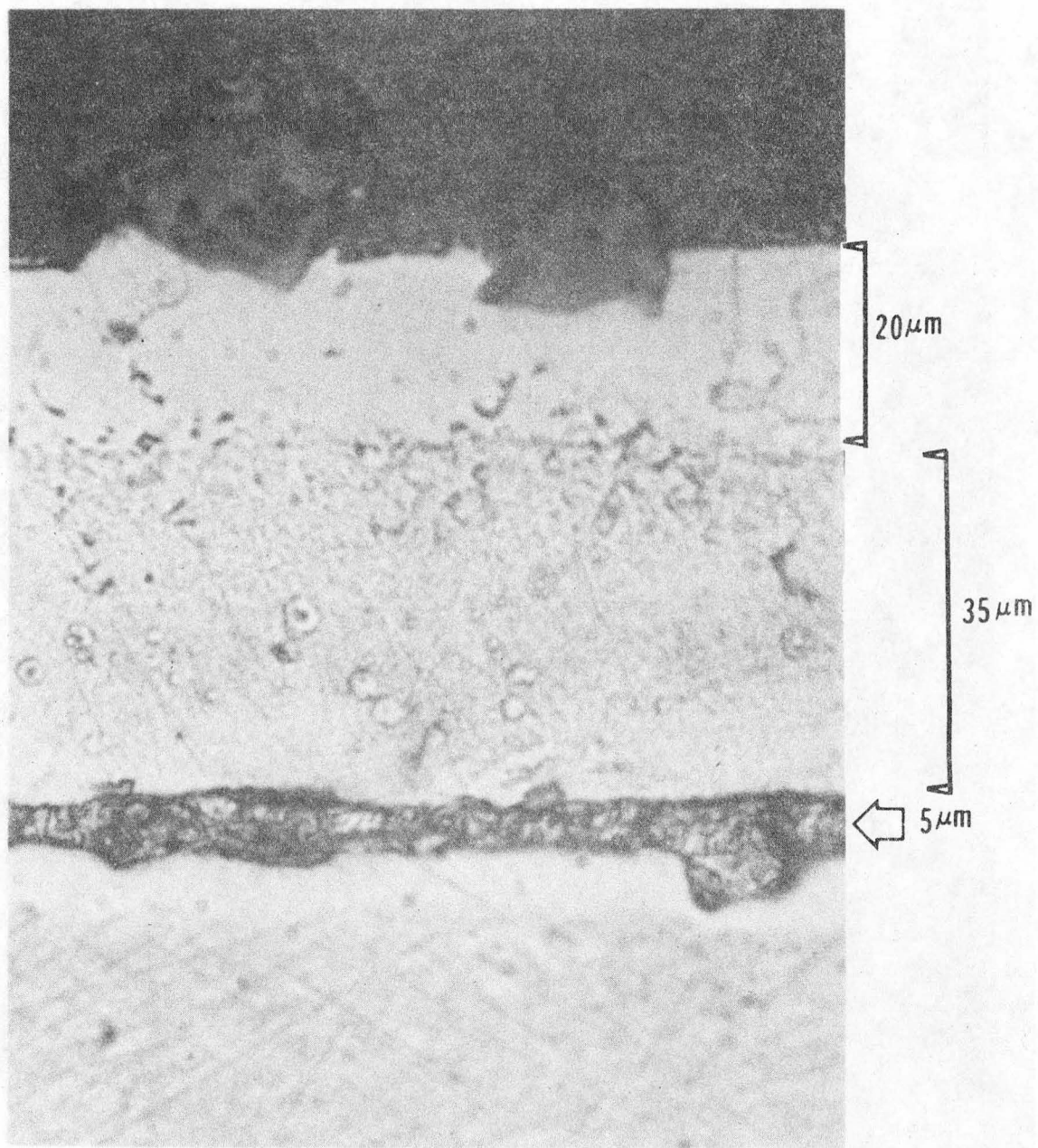


Figure 4

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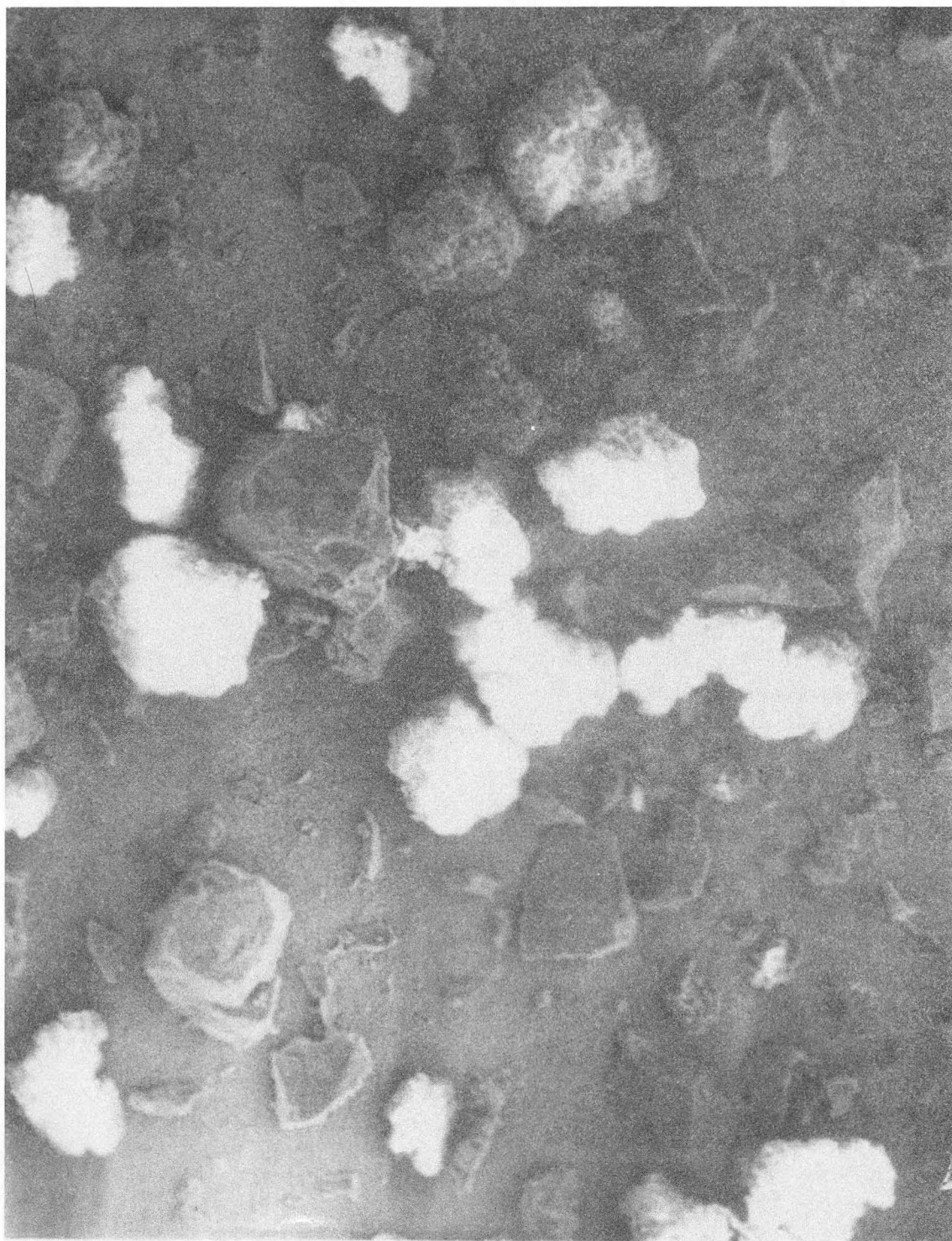


Figure 5

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Figure 6

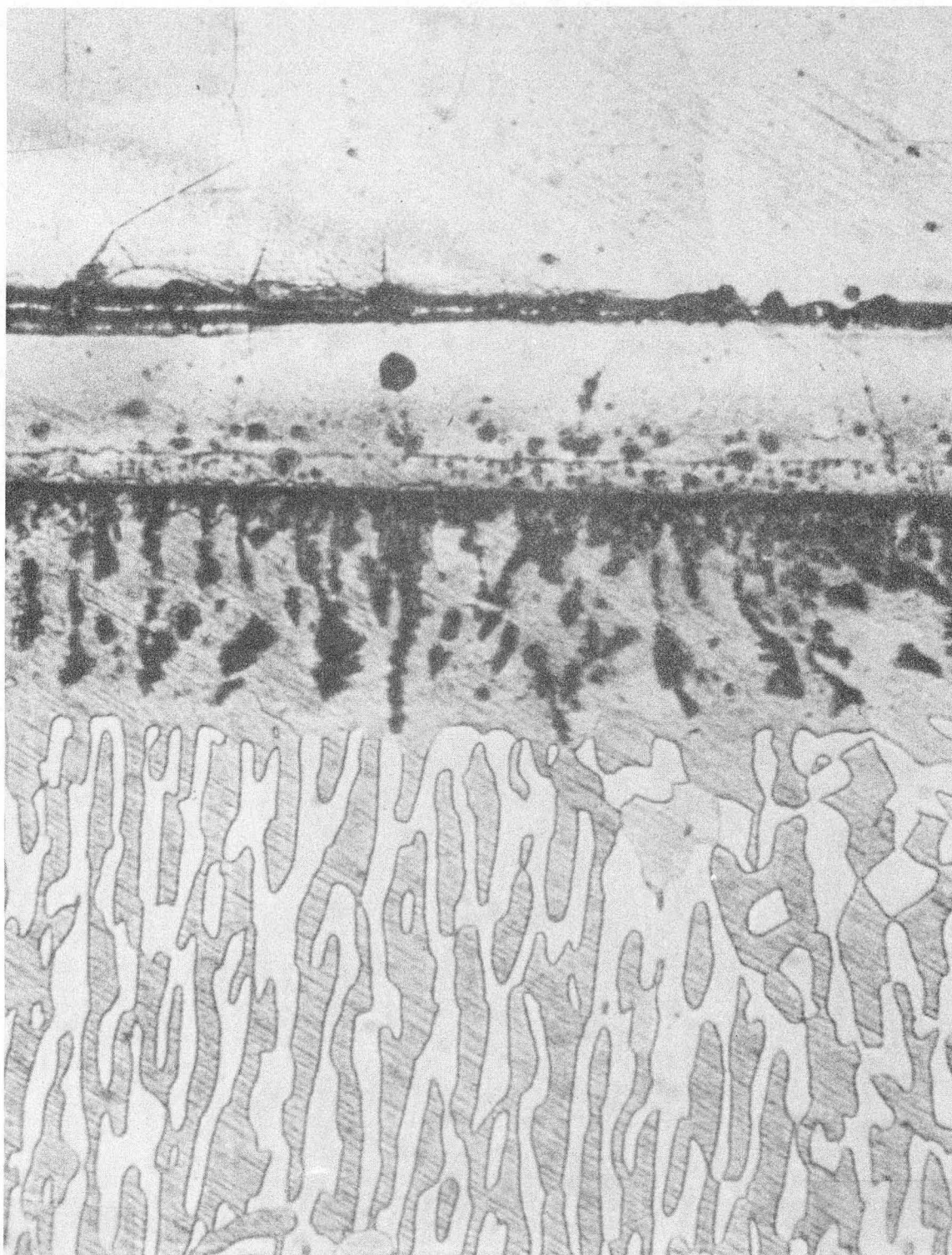


Figure 7

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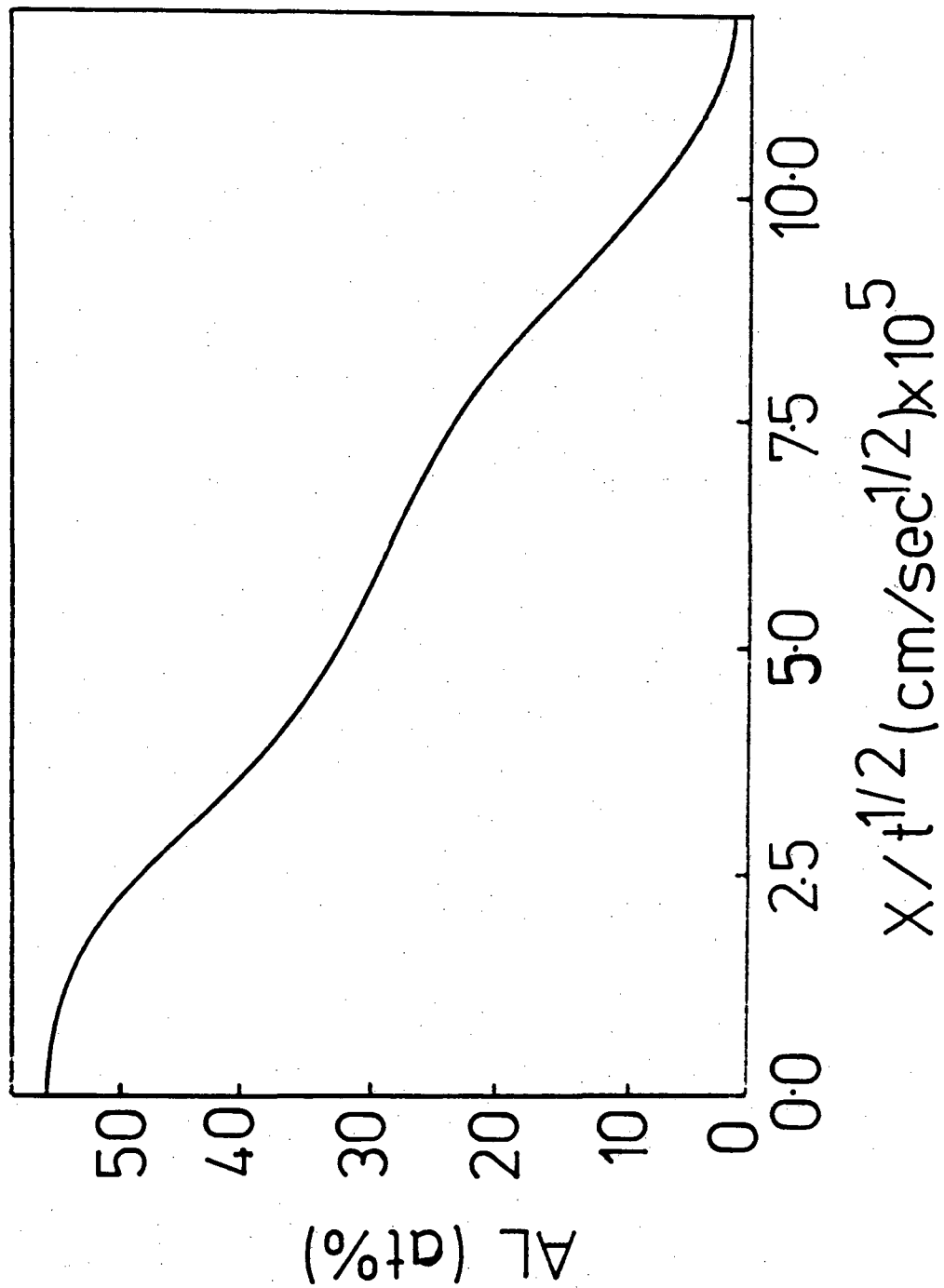


Figure 8.

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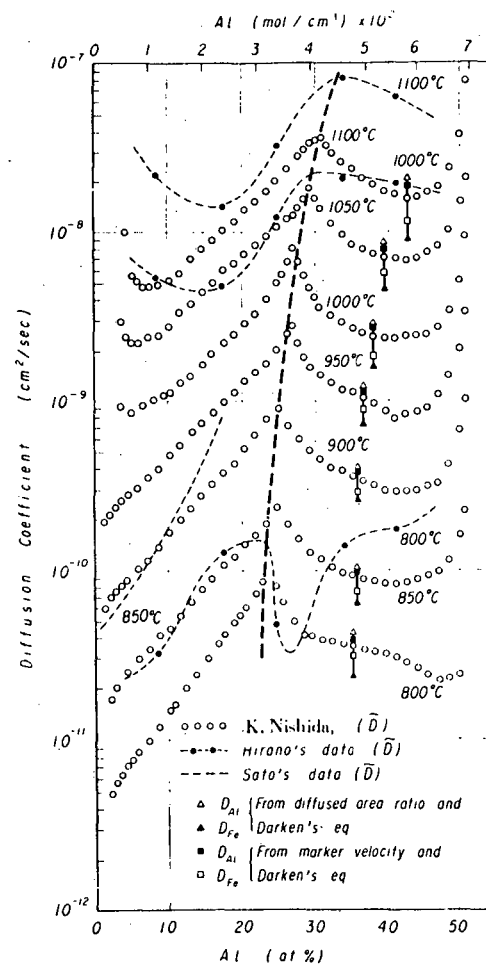
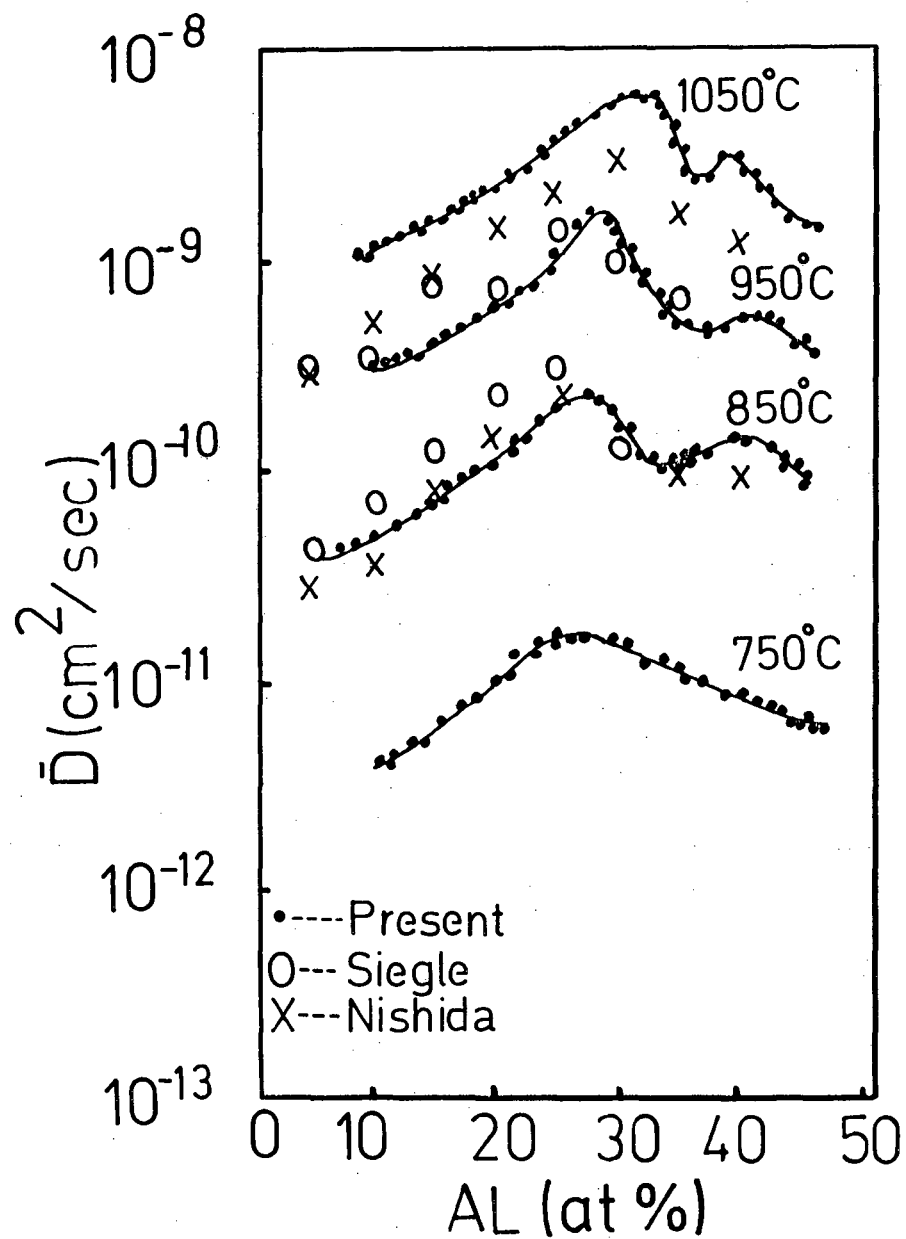


Figure 9.

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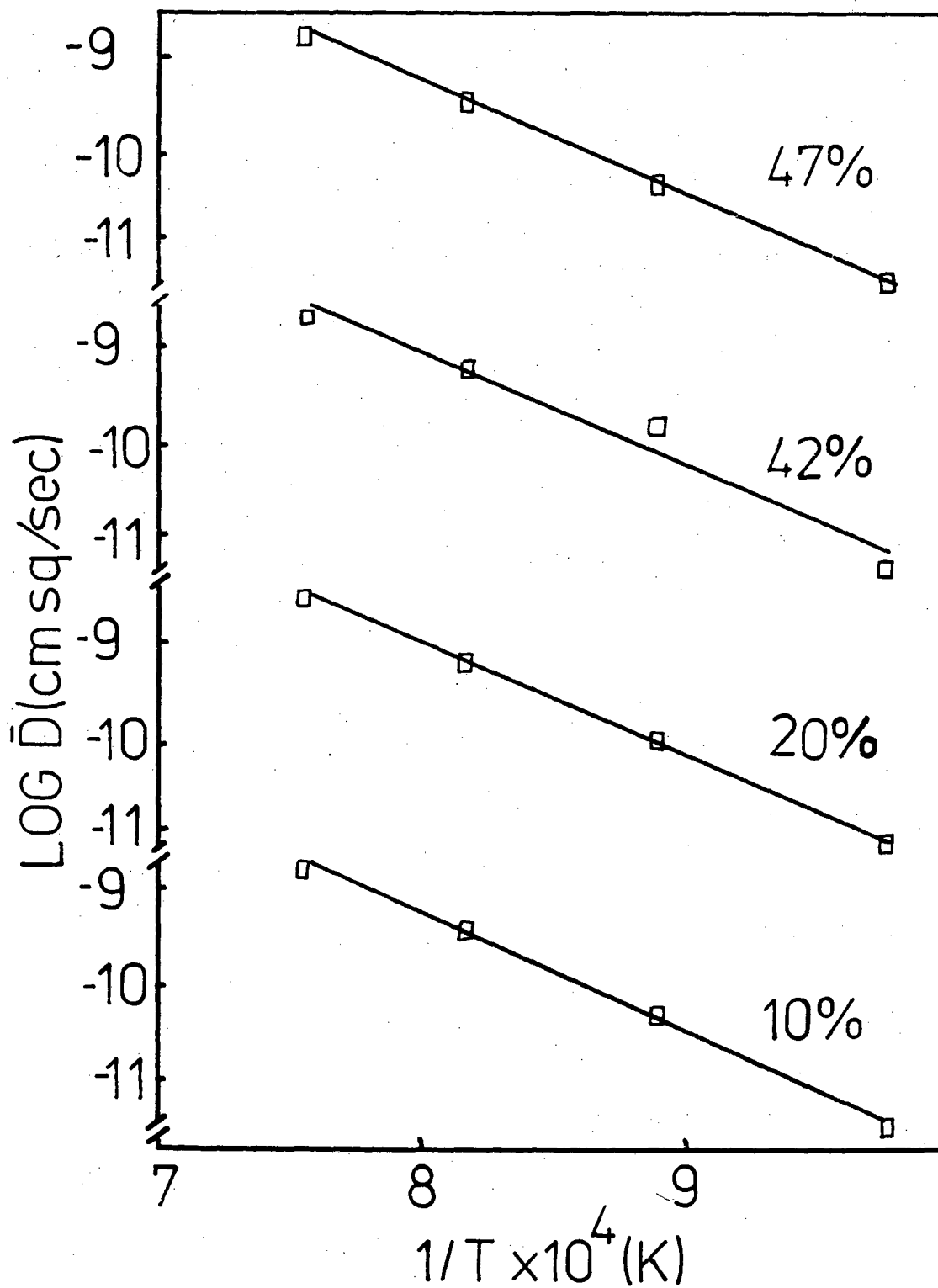


Figure 10.

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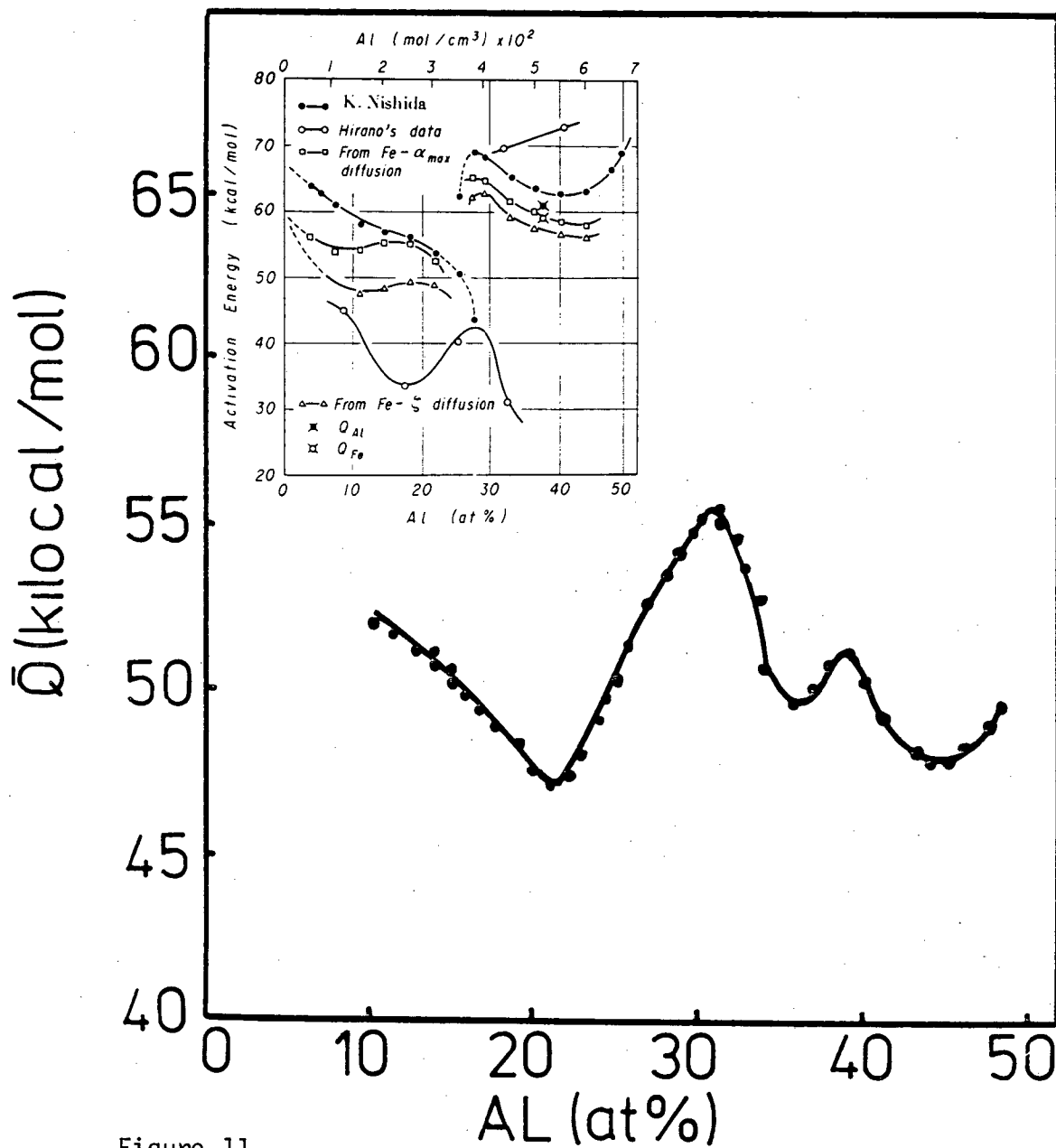


Figure 11.

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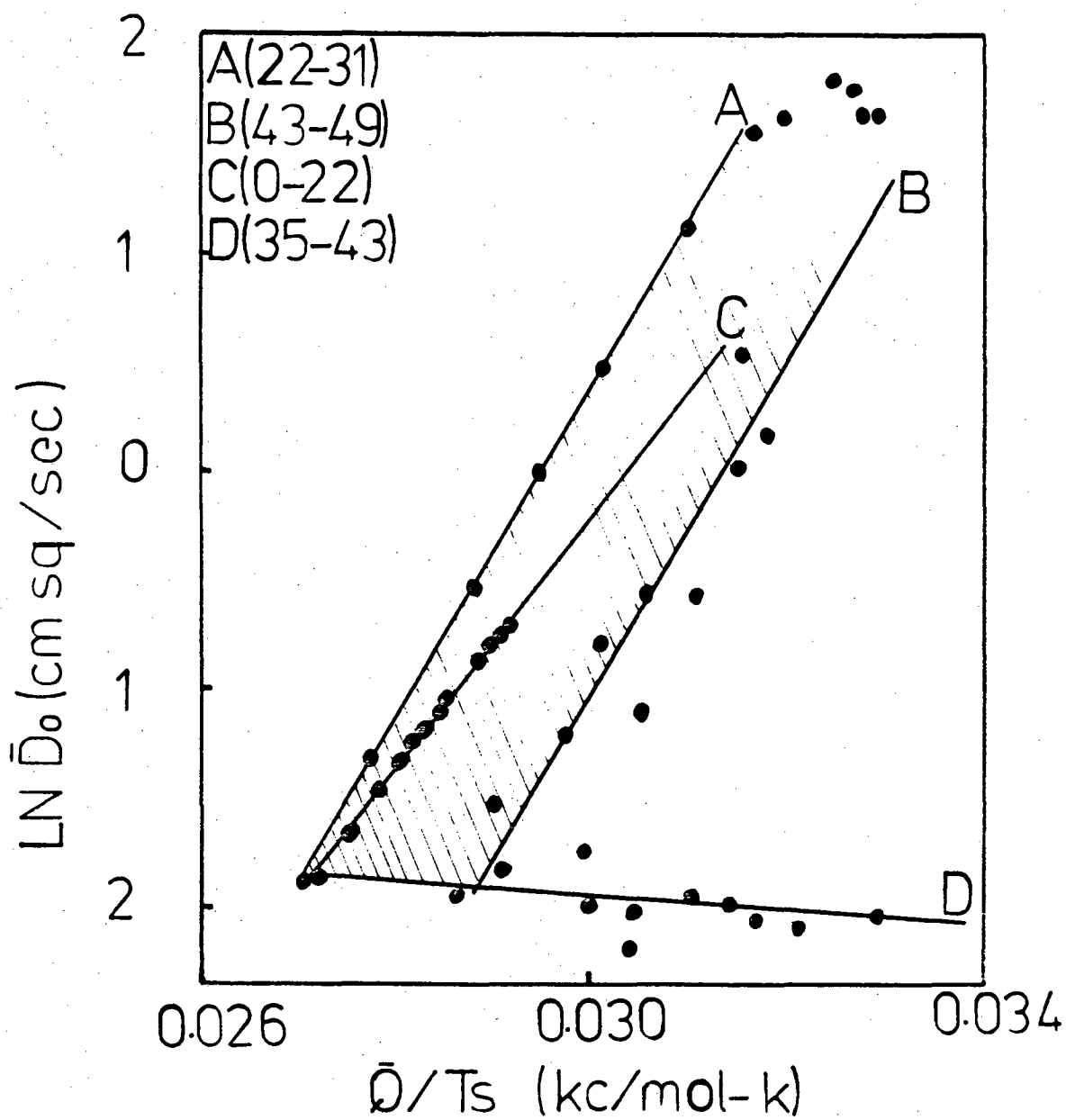


Figure 12.

XBL 819-1854

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