

## REACTION DIFFUSION IN THE SILVER-ZINC AND SILVER-ALUMINUM SYSTEMS\*

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Date: 6-18-69

## ABSTRACT

Multiphase diffusion was investigated in the silver-zinc and silver-aluminum binary systems using metallographic and electron microprobe techniques. Diffusion couples in the silver-zinc system were prepared by electroplating silver onto coupons of a  $\beta$ -AgZn alloy (62.2% Ag), and diffusion behavior was studied at 600 and 650° C. Couples in the silver-aluminum system were prepared by electroplating silver onto coupons of a  $\zeta$ -AgAl alloy (87.7% Ag) and diffusion measurements were made between 400-600° C. Significant deviations from equilibrium compositions were observed at the moving interphase boundary in each couple. The nucleation of a non-equilibrium silver-rich phase was observed at the location of the initial interface in many of the Ag/ $\zeta$ -AgAl couples.

## INTRODUCTION

The objective of this research was to study the chemical compositions at moving interfaces between phases in multi-phase diffusion couples. Earlier research<sup>1</sup> with copper-aluminum,  $\alpha/\beta$ , couples established that the  $\alpha$  phase adjacent to the moving interface was supersaturated with respect to aluminum, the more mobile species. These deviations were interpreted in terms of the driving force required for the phase transformation ( $\alpha$ , fcc $\rightarrow\beta$ , bcc) at the interface.

The magnitude of the compositional deviation at a moving interface may depend on the nature of the reaction occurring at the interface. Consequently, two types of interfaces have been studied: Type I,  $\alpha_1/\alpha_2$ , an interface formed by two phases of the same crystal structure but with different chemical compositions; and Type II,  $\alpha/\beta$ , an interface formed by two phases which have different crystal structures and different chemical compositions. Experimental results obtained with Type II interfaces only will be presented in this paper.

## EXPERIMENTAL PROCEDURES

Two systems furnishing interfaces of Type II were studied: Ag-Zn and Ag-Al. Alloys of  $\beta$ -AgZn (bcc) and  $\zeta$ -AgAl (hcp) were prepared from pure materials and sectioned into coupons. These coupons were electroplated with silver to form the diffusion couples. A portion of each couple was retained to use as a non-diffused standard. Diffusion anneals were carried out in a vertical tube furnace under flowing argon. The furnace was equipped for direct quenching into iced brine.

Concentration-distance profiles were obtained for each couple using an A. R. L. electron microprobe. Interface compositions were obtained from these concentration profiles by extrapolation of the curves to the interface. Figure 1 shows an example of a typical concentration profile and the tangents which were extrapolated to obtain the interface compositions. The location of the interface in the diffusion couple is determined as the midpoint of the linear portion of the profile in this region. The "effective beam diameter" is determined from the curved portion of the concentration profile across a nondiffused interface in the standard. Only the portion of the concentration profile which is outside of the "effective beam diameter" region was used to obtain the interface compositions. A number of concentration profiles were determined for each couple, and both profile and point-count modes were used in the analyses. Intensity levels were standardized against pure materials and intensity-concentration curves were calculated.

## RESULTS

A. Ag/ $\beta$ -AgZn Couples.

Figure 2 shows the equilibrium diagram for the Ag-Zn system, ( $\alpha$  field is fcc,  $\beta$  is bcc). The  $\beta$  alloy used to prepare the couples contained 62.3 wt % Ag and 37.7 wt % Zn.

Figure 3 is a photomicrograph of a  $\text{Ag}/\beta\text{-AgZn}$  couple annealed at  $600^\circ\text{C}$  for 1 hr. The non-diffused standard for the sample is shown at the left. Prominent lines of diffusion voids in the  $\beta$  phase mark the approximate location of the initial interface. The appearance of the  $\alpha/\beta$  interface shows considerable irregularity and a color change from white in pure silver to tan where the  $\alpha$ -Ag solid solution begins is readily observable. Figure 4 is a microprobe trace across the diffusion zone. There is, initially, a steep silver gradient in the  $\alpha$ -solid solution, then the gradient decreases as the  $\alpha/\beta$  interface is approached.

Interface compositions obtained by extrapolation of the concentration profiles are shown superimposed on the  $\text{Ag-Zn}$  equilibrium diagram in Figure 5. The interface compositions approach equilibrium values as length of the diffusion anneal is increased. The non-equilibrium concentrations extend for some distance (approximately 10-15  $\mu\text{m}$ ) outside the region of extrapolation.

In addition to observation of non-equilibrium interface compositions, it was observed that the mobility of the  $\alpha/\beta$  boundary apparently depended on the thickness of the alloy coupon (i.e., the amount of Zn available for diffusion). Couples were prepared from thin (0.008 in., 0.225 mm) and thick (0.050 in., 0.125 cm) alloy coupons, plated with silver annealed at  $600^\circ\text{C}$  for  $\frac{1}{2}$  hr.

Figure 6 shows the thin alloy couple which was annealed at  $600^\circ\text{C}$  for  $\frac{1}{2}$  hr; the non-diffused standard is on the right.

Figure 7 shows the same diffusion couple at higher magnification. The  $\alpha/\beta$  interface is very irregular. However, the interface compositions at different locations were quite consistent (73.2 wt % Ag for  $\alpha$ , 69.0 wt % Ag for  $\beta$ ). The  $\alpha/\beta$  interface moved 10  $\mu\text{m}$  in this couple.

Figure 8 shows the diffusion couple which was prepared from a thick alloy coupon and which also was annealed at  $600^\circ\text{C}$  for  $\frac{1}{2}$  hr; the non-diffused standard is on the right. The  $\alpha/\beta$  interface is quite irregular and the interface compositions were 72.6 wt % Ag for  $\alpha$  and 68.8 wt % Ag for  $\beta$ , compared with equilibrium values of 75 wt % Ag for  $\alpha$  and 71 wt % for  $\beta$ . In marked contrast to the behavior in the thin

couple, the  $\alpha/\beta$  interface in this couple moved approximately 100  $\mu\text{m}$  in the same period of time.

Figure 9 shows the same couple at higher magnification (300X). The appearance of a two-phase region in the diffusion zone is most likely a result of decomposition of  $\beta$  during the quench from the diffusion temperature.

Significant observations for these couples, where only the geometry was varied, are: (1) the amount of boundary motion was tenfold greater for the thick alloy couple; (2) the deviation of interface compositions from equilibrium values was greater for the thick couple; (3) the Ag concentration gradient was steeper in the  $\alpha$  phase of the thick alloy couple. These facts all suggest that the mobility of the boundary between  $\alpha$  and  $\beta$  phases is related to the driving force for interface motion, a measure of the driving force being the excess Zn content of the  $\beta$  phase at the interface.

## B. $\text{Ag}/\zeta\text{AgAl}$ Couples

Figure 10 shows the equilibrium diagram for the  $\text{Ag-Al}$  system. An alloy in the  $\zeta$  field (hcp) of composition 87.7 wt % Ag was prepared and coupons plated with Ag to form the diffusion couples. Diffusion anneals were made at several temperatures between  $480$  and  $600^\circ\text{C}$ . The microstructure of such couples annealed in this temperature range should consist of two phases,  $\alpha$  and  $\zeta$  which are separated by a sharp interface, furthermore the concentration profile should exhibit a smoothly decreasing Ag concentration interrupted by a discontinuity at the  $\alpha/\zeta$  interface.

Figure 11 shows the appearance of a  $\text{Ag}/\zeta$  diffusion couple annealed at  $580^\circ\text{C}$  for  $1\frac{1}{2}$  hr (the non-diffused standard is on the left). Contrary to anticipated behavior, an "intermediate phase" has formed between the  $\alpha$  Ag solid solution and the  $\zeta$  alloy. Figure 12 shows the microprobe traces for Ag and Al across this diffusion zone. At the "intermediate phase," a sharp increase in Ag concentration occurs and a corresponding decrease is observed in the Al concentration. In a binary system the activity increases monotonously with composition and in this system, Al, the more mobile species, must be diffusing down an activity gradient.

Consequently, if true binary diffusion is operating, the dip in the Al concentration represents an instability. Thus this couple cannot be acting as a true binary system. It must be ternary or higher order. An additional component could be the excess vacancy concentration. Contamination of the initial interface during plating must always be considered but there were no discrepancies in the probe analyses which indicate that there was no significant amount of impurities present. Where the phase had nucleated, thickness of the "intermediate phase" increased with time. However, in several samples the nucleation was spotty and there were many locations along the diffusion interface where no "phase" was observed. At these places the concentration profiles appeared normal.

#### SUMMARY:

The following observations can be made as a result of this experimental work:

1. Deviations from the equilibrium compositions were observed at the moving  $\alpha/\beta$  interface in the Ag/ $\beta$ -AgZn couples. These deviations were significant for short anneals and as annealing time increased, the compositions at the diffusion interfaces approached the equilibrium values.
2. Mobility of the boundary in the Ag/ $\beta$ -AgZn diffusion couples appeared to be related to the driving force (the excess Zn in the  $\beta$  phase).
3. In the Ag-Al system a particularly striking example of a non-equilibrium state was observed. Ag/ $\zeta$  couples annealed at 580°C contained an "intermediate phase" occurring between the  $\alpha$  and  $\zeta$  phases. The concentration of Ag increased sharply in this phase, contrary to requirements that the Ag concentration must decrease monotonously across the couple. This behavior may be rationalized by considering these couples as ternary (or higher order) systems where one of the important components is possibly the excess vacancy concentration.

#### REFERENCE

1. J. R. Eifert, D. A. Chatfield, G. W. Powell and J. W. Spretnak, *Trans. AIME*, **242**, 66(1968)

\* Work performed under National Science Foundation Grant No. GK-4118

† Work performed as partial fulfillment of the requirements for a PhD in Metallurgical Engineering, Ohio State University, Columbus, Ohio. This author is presently employed at Mound Laboratory, which is operated by Monsanto Research Corporation for the U. S. Atomic Energy Commission under Contract No. AT-33-1-GEN-53.

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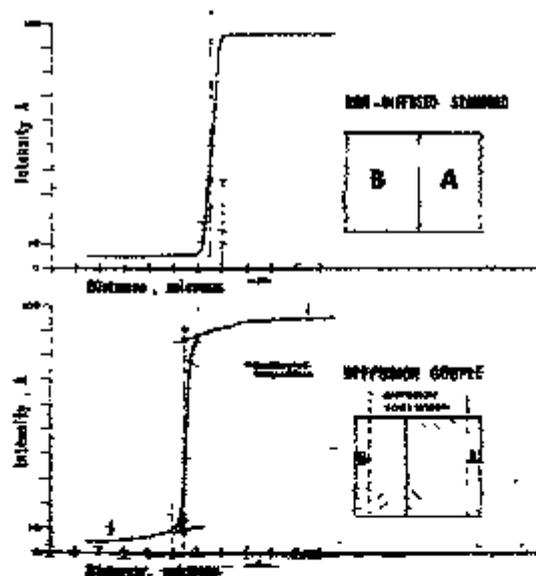


Figure 1. Extrapolation procedure for the determination of interface compositions

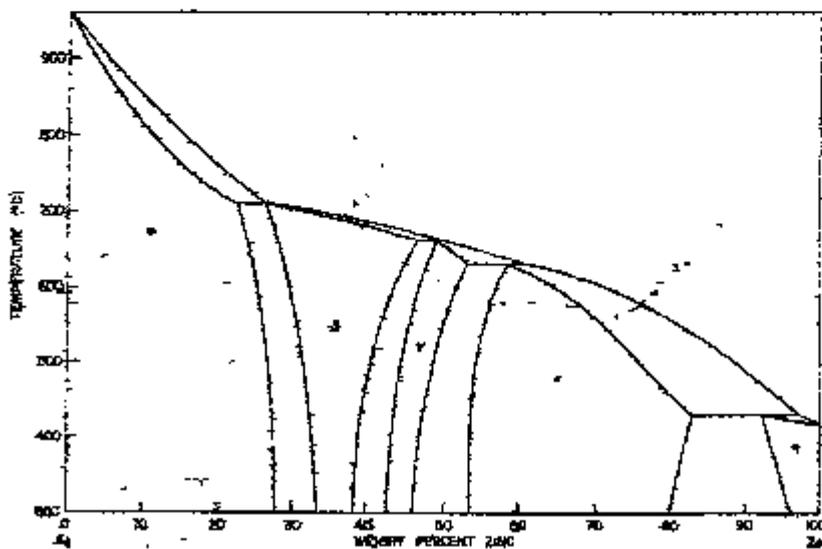


Figure 2. Equilibrium diagram of the Ag-Zn system

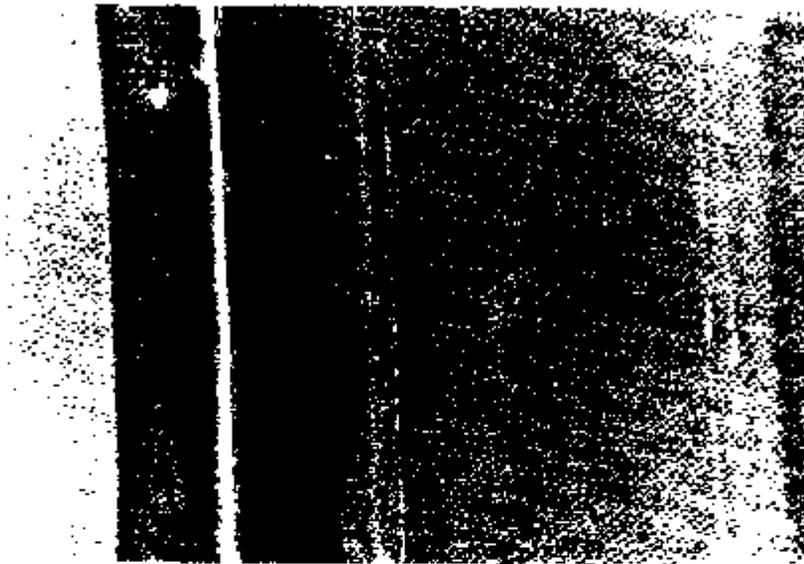


Figure 3. Photomicrograph of Ag/β-AgZn diffusion couple annealed at 600°C, 1 hr and non-diffused interface, 75X

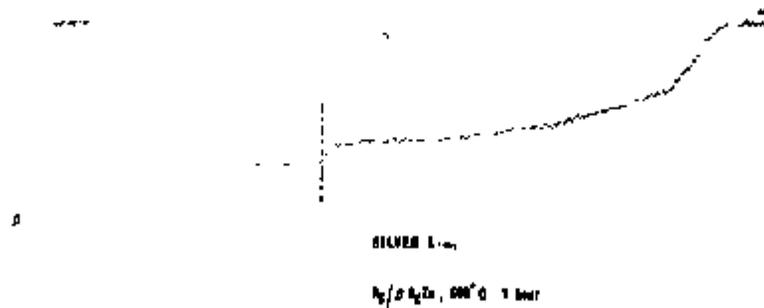


Figure 4. Microprobe trace for Ag L- $\alpha$  radiation across the diffusion zone of the 600°C - 1 hr couple.

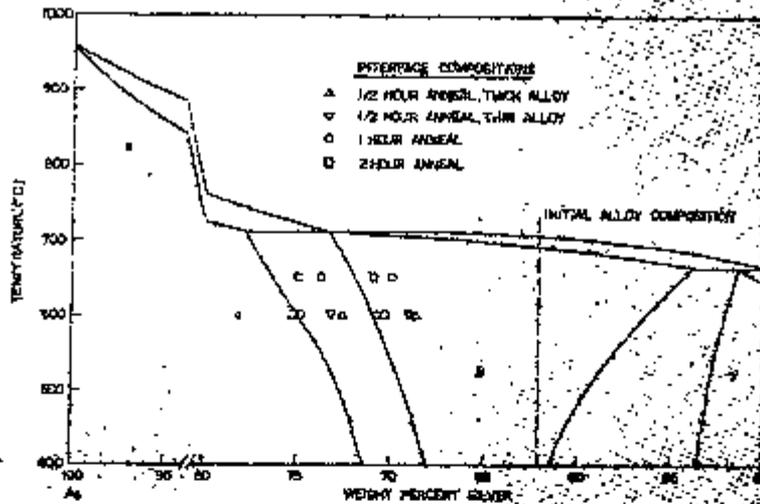


Figure 5. Superposition of interface compositions on the Ag-Zn equilibrium diagram

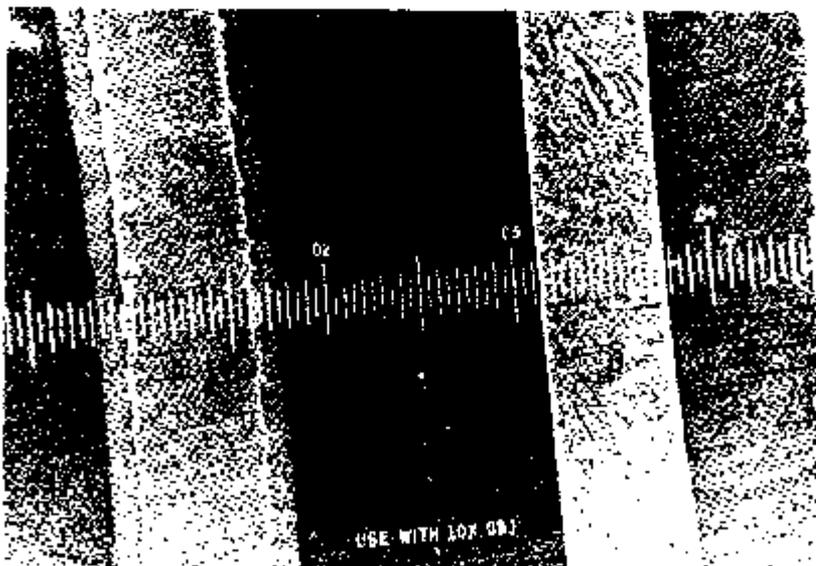
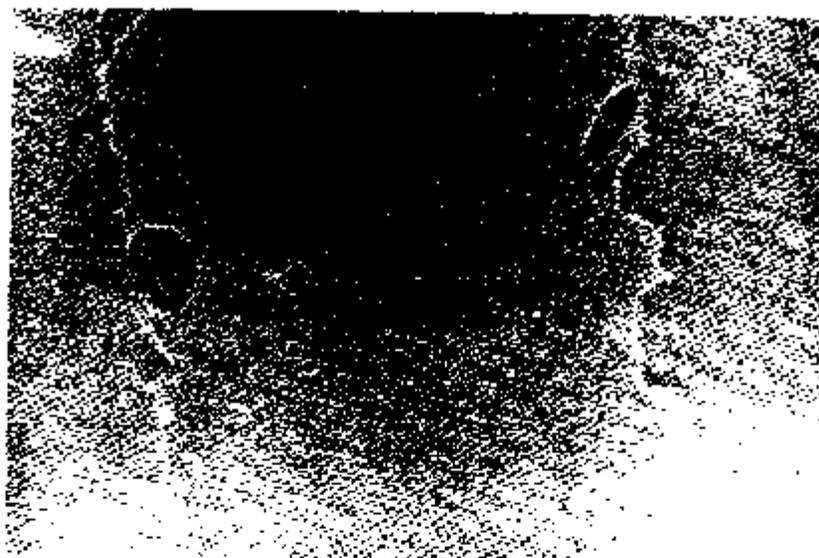
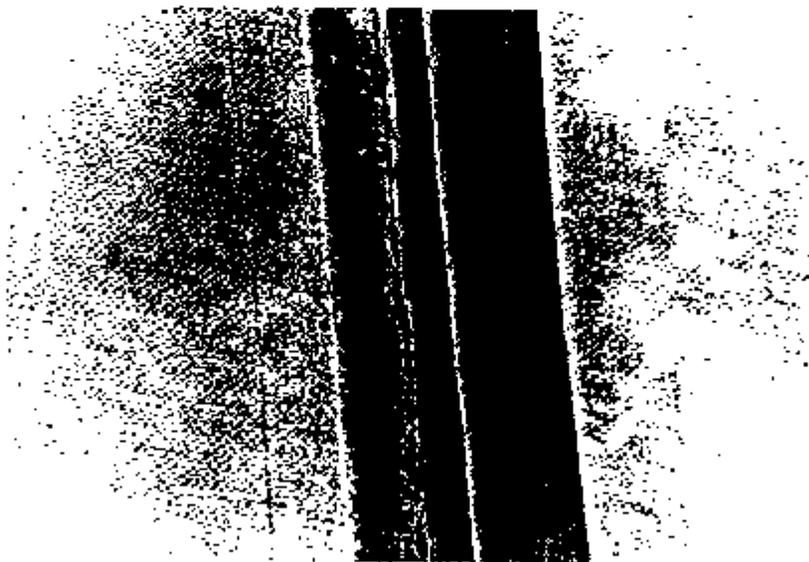


Figure 6. Photomicrographs of Ag/β-AgZn diffusion couple annealed at 600°C; 1/2 hr - (thin alloy) and non-diffused standard, 60X



*Figure 7. Photomicrographs of Ag/ $\beta$ -AgZn diffusion couple, 600°C - 1/2 hr, (thin alloy), 300X*



*Figure 8. Photomicrographs of Ag/ $\beta$ -AgZn diffusion couple - annealed at 600°C - 1/2 hr, (thick alloy) and non-diffused standard, 75X*

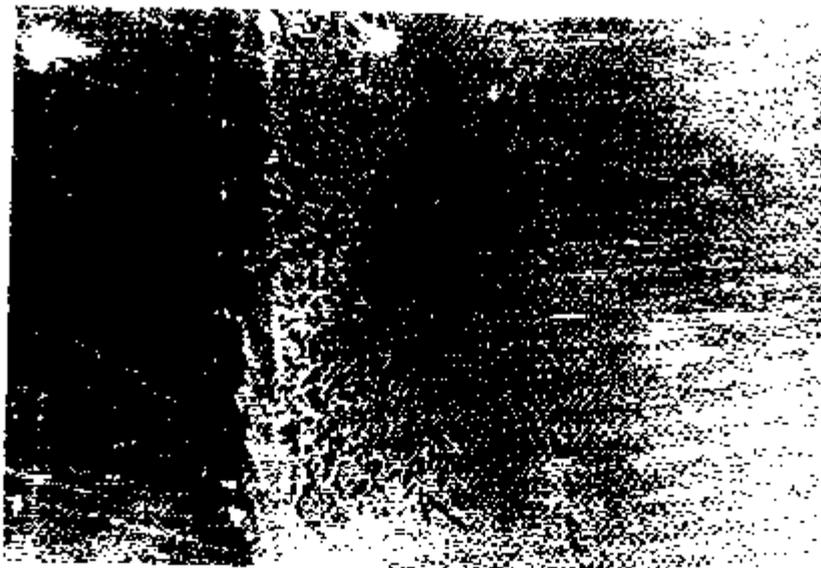


Figure 9. Photomicrograph of Ag/β-AgZn diffusion couple - 600°C - 1/2 hr, (thick alloy), 300X

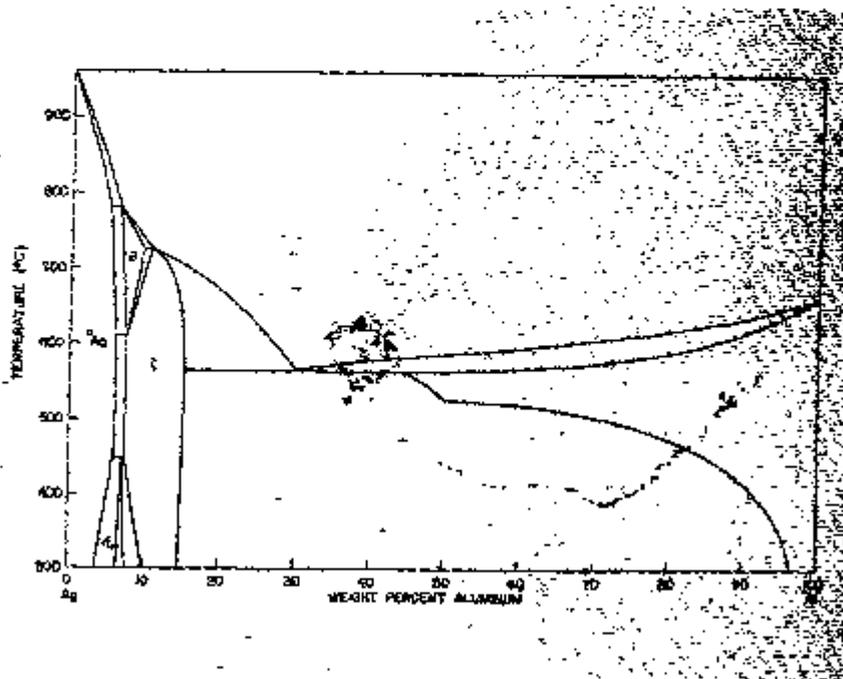


Figure 10. Equilibrium diagram for the silver-aluminum system.

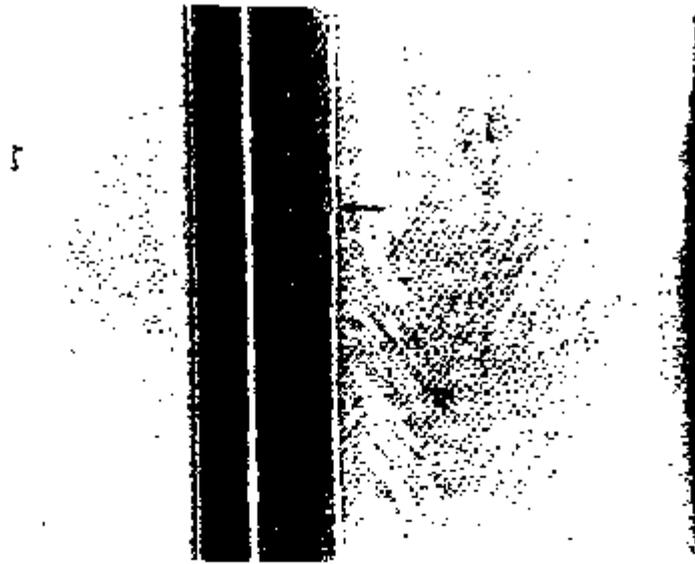


Figure 11. Photomicrograph of a Ag/ξ diffusion couple diffused at 580°C for 1-1/2 hr, and non-diffused standard, 75X

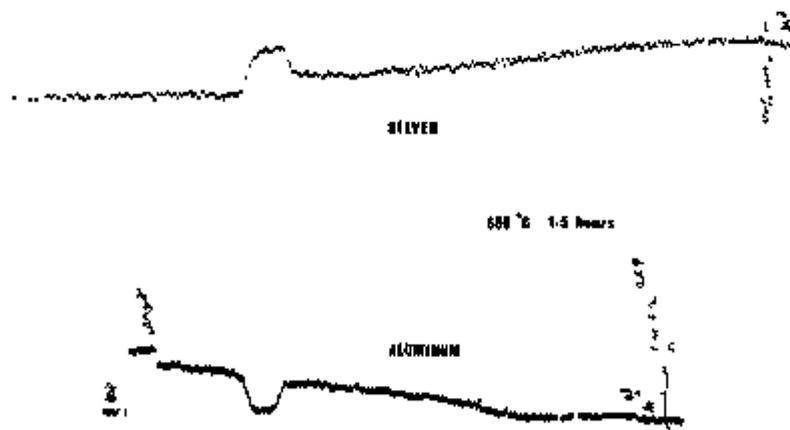


Figure 12. Microprobe traces for Ag  $L_{\alpha_1}$  and Al  $K_{\alpha}$  radiation across the diffusion zone in the 580°C - 1-1/2 hr couple.