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Grain Boundary Diffusion in a Body-Centered Cubic Lattice

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ABSTRACT

Oriented bicrystals of a 3% silicon iron alloy were prepared with a common [011] direction, and were used in a study of intergranular diffusion in the body-centered lattice. The penetration of iron at the grain boundary during diffusion was obtained by an autoradiographic technique. The penetration was found to be orientation dependent, with no preferential grain boundary diffusion being observed for relative angles of disorientation below about 10°. In general the penetration increased up to a disorientation of 86° with a broad minimum in the neighborhood of 50°. The results can be interpreted in terms of the density of atoms of misfit at the grain boundaries although little correlation seems to exist between penetration and grain boundary energy at the cusp positions.

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INTRODUCTION

The phenomenon of grain boundary diffusion in metals has been known for many years and has been reported in the literature occasionally. Recently several more detailed studies of grain boundary diffusion have been made, both experimental and theoretical, stimulated by the desire for more information on the structure of the grain boundary.

Mehl(1) in 1936 reviewed the evidence on grain boundary diffusion up to that time. In general this evidence consisted of observations of the variation of over-all diffusion coefficients in polycrystalline materials with grain size. The observation of larger diffusion coefficients with smaller grain size was taken to indicate that diffusion occurred at the grain boundary more rapidly than in the lattice of the grains themselves. More recently metallographic and radiographic evidence has been presented to show preferential intergranular diffusion. Keller and Brown(2) obtained photomicrographs showing the copper enrichment of grain boundaries of the aluminum cladding on Alclad sheet by diffusion. Barnes(3),(4) has made an interesting micrographic study of the diffusion of copper into nickel, with preferential penetration at many grain boundaries but not at twin boundaries of the nickel. Hoffman and Turnbull(5) used a radioactive tracer technique to study the rate of self-diffusion of silver which exhibited a grain size effect. They also made a contact autoradiograph of a sectioned specimen which showed that preferential grain boundary penetration had occurred.

The orientation dependence of the diffusion of silver into columnar copper was investigated by Achter and Smoluchowski(6) using a metallographic technique. Diffusion couples of 4% silver copper alloy versus columnar copper were diffused at temperatures from 673° to 725°C. These couples were sectioned parallel to the interface (normal to the columnar [001] direction) at successively greater distances and the limit of intergranular penetration between each pair of grains was determined metallographically. The results indicate that the grain boundary diffusion is markedly dependent on the relative orientation of the grains forming the boundary. It was found that if θ, the angle between the (100) planes including the grain boundary, was less than 20° or greater than 70° there was no preferential grain boundary diffusion observed; if θ lay between 20° and 70° there was preferential diffusion at the grain boundary with a maximum at θ near 45°. Flanagan and Smoluchowski(7) investigated the diffusion of zinc into columnar copper in a similar manner. Their results confirm the influence of angle of disorientation between grains on intergranular diffusion and indicate an angular dependence of activation energy for the process. This led to a model(8) for the structure of grain boundaries for angles of disorientation higher than the range of applicability of the classical dislocation model.

Couling and Smoluchowski(9) have studied the anisotropy of diffusion in tilt type grain boundaries using bicrystals of copper having parallel [100] axes and angles of disorientation in the range from 0 to 90°. In addition to dependence on the angle of disorientation, an anisotropy was observed in the amount of penetration at the boundary; that is, the penetration varies with the direction of diffusion in the plane of the boundary. Theoretical

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treatments of grain boundary diffusion under the assumption that the grain boundary has a uniform "thickness" and a characteristic diffusion coefficient which has a constant ratio to the volume diffusion coefficient have been given, first approximately by Fisher(10), and later more exactly by Whipple(11).

In view of the fact that the body-centered cubic lattice is a less closely packed arrangement of atoms than the face-centered cubic lattice, one could expect that there would be less difference between the mobility of atoms in the grain and in the grain boundary of a body-centered cubic lattice than in a face-centered lattice. If such is the case, one might also expect that preferential grain boundary diffusion would occur to a lesser degree, if at all, in the body-centered cubic material. The investigation described in this paper was undertaken to study the possible variation of grain boundary diffusion in a body-centered cubic lattice with the orientation of the crystals forming the boundary. The availability of a convenient radioactive isotope made a study of grain boundary self-diffusion in iron particularly favorable. Since small amounts of silicon promote growth of large grains in iron it was decided to use this alloy. This implies the assumption that the angle of disorientation does not affect the solubility of silicon in the grain boundary material.

EXPERIMENTAL

Bicrystal specimens were grown by the strain-anneal method from decarburized commercial silicon iron sheet. Strips 1-1/8 inch wide by 10 inches long were cut from 0.030 inch thick sheet of silicon iron supplied through

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the courtesy of the Allegheny-Ludlum Steel Corporation. Chemical analysis of the material was as follows: C 0.022%, Mn 0.043%, P 0.011%, S 0.017%, Si 3.17%, Sn 0.012%, Al trace. The strips were decarburized in an atmosphere of moist hydrogen at a temperature of 850°C for 48 hours. They were then rolled to a thickness of 0.025 inch, and the edges ground parallel to a width of one inch. This was followed by an annealing treatment at 800°C in hydrogen for one hour which resulted in a fine grain size. The strips were strained 2-1/2 percent in tension and the ends cropped to remove the material held in the grips. A short length at one end of each strip was recrystallized by raising it slowly into a furnace in which a steep temperature gradient existed, with the maximum temperature in the furnace (1020°C) being well above that needed for recrystallization. This procedure usually resulted in the formation of several large grains in the area recrystallized. The orientation of those grains which adjoined the unrecrystallized area was determined roughly by the etch pit method(12), and the one having an orientation nearest to that desired, i.e. the (011) plane parallel to the surface, was used as a "seed" in the preparation of a bicrystal with the two grains having predetermined relative orientation. This was done by the general technique outlined by Dunn(13) and described in detail by Dunn and Nonken(14).

The orientation of the selected seed crystal was determined accurately by means of the Laue back-reflection x-ray method. All of the recrystallized material was cut off the strip with the exception of a small amount of the seed crystal which was left on the end of a narrow neck of unrecrystallized material connecting it with the main body of the strip. The seed was then reoriented by twisting and bending the neck (which was locally heated to a dull red heat to prevent further cold-straining) in a jig to make the (011) plane parallel to the surface of the main body of the strip. Again the strip was heated progressively from the seed end causing the seed to grow into the body of the specimen with the desired orientation. The orientation of the crystal was checked by means of the Laue back-reflection method. In order to form a bicrystal, the end of the strip was again cut, leaving seeds at the ends of two necks of unrecrystallized material. These two necks were bent about the (011) pole perpendicular to the surface of the strip so that the [100] directions of the two seeds were the desired angle θ apart and symmetrical with respect to the axis of the strip. Growth of the two seeds into the body of the strip then resulted in a bicrystal from which Laue back-reflection x-ray photographs were made to determine the exact angle θ between the [100] directions and the angle ψ between the (011) poles of the two crystals. The angle ψ was in all cases less than five degrees.

Specimens approximately 3/4 inch square were cut from the bicrystals with the grain boundary roughly parallel to and midway between the edges. The grain boundary as grown was in general far from straight. In order to straighten it and bring it to a stable low energy position, a high temperature annealing treatment was given to the specimens. They were packed flat in a close fitting box machined from silicon iron to prevent loss of silicon by vaporization at the annealing temperature, and the box containing the specimens was heated to 1300°C in an atmosphere of dry argon for one week. The resulting movement of the grain boundary was mostly of microscopic order of magnitude.

The specimens were subsequently prepared for electroplating by polishing both faces on emery paper to grade 3/0. Thickness was checked on a Pratt and Whitney comparator, and variations were held to ± 0.0001 inch in the area to be plated. Electroplating of the specimens was carried out by the general method described by Buffington, Bakalar, and Cohen(15) in which the iron is deposited from ferric chloride in a saturated solution of ammonium oxalate made slightly alkaline with ammonium hydroxide. An area, along the grain boundary, about 5/8 inch long by 1/2 inch wide was plated with iron isotope 55, obtained from the Oak Ridge National Laboratory in the form of ferric chloride solution. This isotope has a half-life of about 4 years and disintegrates by K-electron capture, emitting a low energy x-ray capable of exposing x-ray film. Each specimen was plated with the same amount of radioactive iron solution, to a measured activity of about 5×10^5 counts per minute.

After plating, the specimens were placed face to face in pairs in close-fitting cells of silicon iron for the diffusion treatment. This was carried out in a ceramic tube in an atmosphere of dry hydrogen. Because of the relatively long diffusion periods, no correction was necessary for the heating or cooling time. Temperature was controlled to ± 1° in most cases, with a

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maximum variation of ± 3° from values given. A trial run at 704°C for 144 hours using a specimen having an angle of disorientation θ of 47° showed that preferential grain boundary diffusion was taking place and that a higher temperature or a longer diffusion period would be necessary to produce a suitable penetration. Based on published self-diffusion data for iron(15),(16) and a diffusion period of about one week, it was calculated that a temperature of about 825°C would give a satisfactory amount of volume diffusion. Accordingly the first series of specimens was diffused 176 hours at 827°C. In order to try to get a more pronounced difference between grain boundary and volume diffusion, later runs were made at lower temperatures and for correspondingly longer times; that is, at 810°C for 266 hours at 769°C for 752 hours and 750 hours.

The specimens of the first (827°C) diffusion run were mounted in bakelite and a series of layers was removed from the active face by polishing on emery paper. After each layer was removed, an autoradiograph of the exposed surface was made and the activity of the surface was counted through a slit 0.25 inch by 0.030 inch. It became apparent that it was not possible to polish a specimen so that the plated area was of uniform activity away from the grain boundary, presumably because the specimen could not be kept sufficiently flat during the mounting and polishing operations. Also, the counting times involved became impractically long. It had been hoped that by positioning the slit over the grain boundary and over one of the crystals near the boundary for successive counts, a measure of the greater penetration at the grain boundary

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could be obtained. The differences were so small, however, that they could not be accurately determined. The autoradiographs on the other hand showed the difference between the grain boundary and the volume diffusion quite well, and a good autoradiograph could be made in a reasonable time from a specimen from which layers were removed down to a point where the count was only slightly above background. Therefore it was decided to concentrate on the autoradiographic method for determination of the diffusion penetration. Furthermore, because of the difficulty of sectioning the specimens parallel with the interface it was decided to section intentionally at a small angle with the interface, so that the surface would be below the limit of volume diffusion at the other end. An exposure time of one week was chosen for determination of maximum penetration, Kodak No-Screen x-ray film was ued for the autoradiographs, and the development of the film was standardized. Figure 1 shows an autoradiograph of a slope sectioned specimen.

The location of the last visible trace of the grain boundary on the autoradiograph was determined by inspection, and its position transferred to the surface of the specimen itself by micrometer measurement. The thickness of the specimen at this location was then measured with a dial gage comparator, and the penetration calculated by difference from the original thickness to the nearest 0.0001 inch.

RESULTS AND DISCUSSION:

The depth of penetration at the grain boundary as determined by the above procedure is plotted, for the temperatures 769° and 810°C, in figure 2. These results were obtained by the slope sectioning technique and are considered more reliable than the results from the set of samples diffused at 827° which were sectioned approximately parallel to the interface. A comparison of the two runs at 769°C indicates the reproducibility of the measurements.

The corresponding amount of volume diffusion could not be determined accurately because of the difficulty in evaluating the effect of the relative areas involved in exposing the autoradiographs. The required concentration of radioactive atoms in the grain boundary would need to be much higher to give a visible image on the autoradiograph than that in the relatively broad expanse of lattice. This points out the expected low preference for grain boundary diffusion in a body-centered metal as compared to a face-centered metal. A rough value for the volume diffusion is about 0.004 in. The effect of grain boundary direction was not determined because of the frequent irregularity of the grain boundary. No preferential grain boundary penetration was observed for $\theta = 6$ and 9 degrees. Although there is considerable scatter at some angles of disorientation, several points of interest are apparent on inspection of figure 2. The first observation is that specimens having an angle of orientation difference below about 10° show no preferential grain boundary diffusion, while those with θ equal to 15 or 16 degrees do. Evidently at some intermediate angle the grain boundary diffusion becomes enough greater than lattice diffusion to be detected by the experimental procedure used. This confirms the general character of the angular dependence of grain boundary penetration as observed earlier by Achter, Flanagan, Couling and Smoluchowski(6),(7),(9) although here the uncertainty in the value of the volume diffusion makes the critical angle much less pronounced. The existence of this angle was interpreted(8) in terms of transition from single dislocations to rod-like regions of distorted lattice at angles higher than the critical angle. It should be pointed out, however, that recent work of Turnbull and Hoffman(17) seems to indicate presence of preferential diffusion along dislocations. Another fact to be remembered in interpreting figure 2 is that the small angle tilt type boundary between body-centered cubic crystals with a common [011] direction is not made up solely of pure edge dislocations but the dislocations contain a screw component. The effect of the screw component on diffusion at the boundary is not known but is evidently not great in this case.

Another striking feature of the plot in figure 2 is the broad minimum of grain boundary penetration near $\theta = 50^\circ$. Qualitatively this is similar to the slight minima of penetration observed by Achter(6) and by Couling(9) in the Cu-Ag system. Quantitatively the broad minimum in figure 2 is much more pronounced and more reproducible than those observed on copper in spite of the considerable scatter of the experimental points in this region. It has been often suggested that minima of grain boundary energy and of grain boundary diffusion penetration occur whenever the distance ρ between atoms common to both grains is small. On this model the minimum for the Cu-Ag system has been interpreted in terms of coincidence of a (210) plane of each grain with a symmetrical grain boundary. The possible energy cusps for our type of grain boundaries are listed in Table I in order of increasing δ, thus, according to Read and Shockley(19), in order of increasing energy. For completeness all angles up to 180° are included although only those up to about 90° have been investigated. Read and Shockley seem to find a rough quantitative correlation between δ and the depth of energy cusps as observed by Dunn and Lionetti(20) although they consider only the cusps (112), (332), (111), (334) and (221) and reverse the sequence of the (111) and (332) cusps. The coincidence of the normal twinning plane (112) with the grain boundary would lead to a strong minimum at $\Theta = 109^\circ$ which lies outside of the range of our specimens but qualitatively agrees with the maximum penetration observed at about $\Theta = 76^\circ$ and the general shape of the curve. As is well known, ideal twin boundaries do not show preferential diffusion(4, 18). The 50° minimum agrees very well with the next cusp of the (332) planes. No other cusps are clearly distinguishable. This is in contrast to the energy measurements(20) which for angles below 90° show the deepest minimum at 70° and a secondary minimum near 40°; presumably due to the (221) planes.

It appears thus that whether or not there is correlation between δ and the depths of the energy minima there is little correlation between the depths of the energy minima and penetration minima though their occurrence at or near

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the cusps angles indicates certain common features. An inspection of the probable structure of the grain boundaries at the various cusp angles as shown in figure 3 indicates, however, a possible way of explaining the various penetrations. It appears that there is a pronounced difference in the "openness" of the various grain boundaries which does not seem to be related in any simple way to δ. In figure 3, atoms drawn full are those which occupy essentially normal lattice positions. Some of them as atoms B for $\theta = 39^\circ$, may have a slightly tight fit but they have at least half of their normal contingent of first and second neighbors in proper positions. For $\theta = 86.6^\circ$, atoms A would be squeezed and would have less than half the normal number of first and second neighbors and are thus considered replaced by a mobile atom. These mobile atoms do not belong to any specific grain and are indicated by dotted circles. Certain of the openings or channels are too small to accommodate any such atoms of misfit. Thus it seems plausible to try to relate the penetration to the density m of atoms of misfit in the various grain boundaries. The values of m are listed in Table I together with the best estimates of the grain boundary penetration p beyond the limit of volume diffusion. Figure 4 shows the plot of m versus p. Question marks near the points for the (556) and (776) cusps indicate that these penetration values are much less certain than for other cusps. Apparently in spite of a large scatter of points there is an approximately linear correlation between m and p. As mentioned before, no such correlation exists with δ or with the depths of the energy minima. In particular the relatively low value of penetration near 39° which is a high δ cusp and the relatively high penetration near 70° which is a low δ cusp seem to be understandable in terms of the density of atoms of misfit. A further check on this interpretation may be provided by extending the measurements to higher angles. In particular at $\theta = 164^\circ$ one would expect a cusp in spite of a rather large δ.

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TABLE I

Grain Boundary plane	Distance between common atoms (in a_o) δ	Angle between grains in degrees	Number of channels of misfit per δ	Number of misfit atoms per δ	Density of misfit atoms m	Observed penetration beyond volume diffusion in 10^{-3} in.
1 1 2	0.87	109.5	0	0	0	—
3 3 2	1.66	50.5	0	0	0	.07
1 1 6	2.28	153.8	1	1	.438	—
1 1 1	2.45	70.6	1	1	.408	3.0
5 5 2	2.60	31.6	1	1	.385	2.5
1 1 4	3.00	141.1	2	1	.333	—
5 5 6	3.28	80.6	2	1	.305	3.0?
7 7 2	3.54	22.8	1	2	.564	2.7
1 1 10	3.54	163.9	1	1	.282	—
3 3 10	3.84	134.1	2	3	.782	—
7 7 6	4.09	62.4	2	2	.489	2.2?
3 3 4	4.13	86.7	2	2	.485	3.0
2 2 1	4.24	39.0	1(2)	1(2)	.236(.472)	1.8

FIGURE CAPTIONS

Fig. 1	Negative of an autoradiograph of a slope-sectioned bicrystal (light areas indicate presence of radioactive isotope). Original interface greatly overexposed to show grain boundary penetration.
Fig. 2	Depth of grain boundary penetration as a function of angle between cubic directions of the two grains.
Fig. 3	Structure of grain boundaries at the most important cusp positions ($0^\circ < \theta < 90^\circ$). (The atom just above the vertical arrow in the drawing for $\theta = 86.6^\circ$ should have been drawn somewhat lower so as to have only two nearest neighbors in the plane of the drawing.)
Fig. 4	Grain boundary penetration p as a function of the density of atoms of misfit m at cusp angles.
Table I	Structure of grain boundaries at cusp positions ($0^\circ < \theta < 180^\circ$) and observed penetrations.

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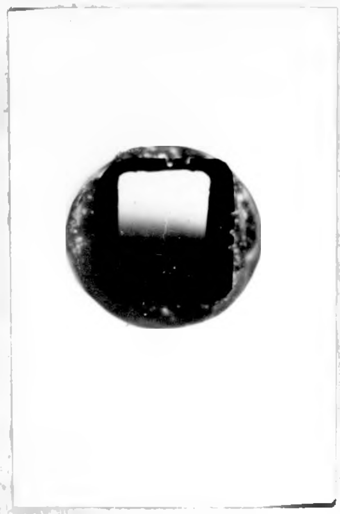

Fig. 1

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Fig. 2

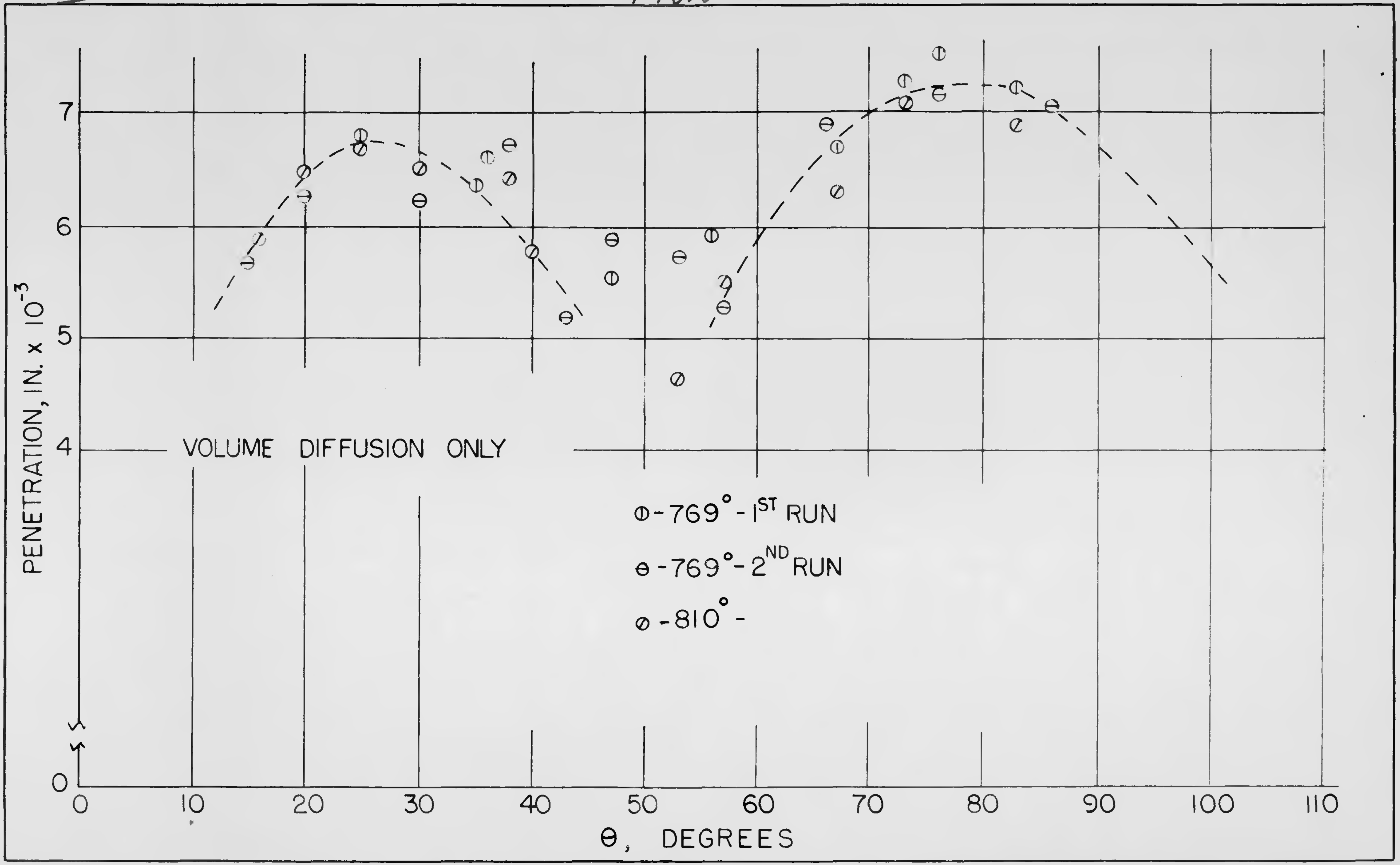

Fig. 2

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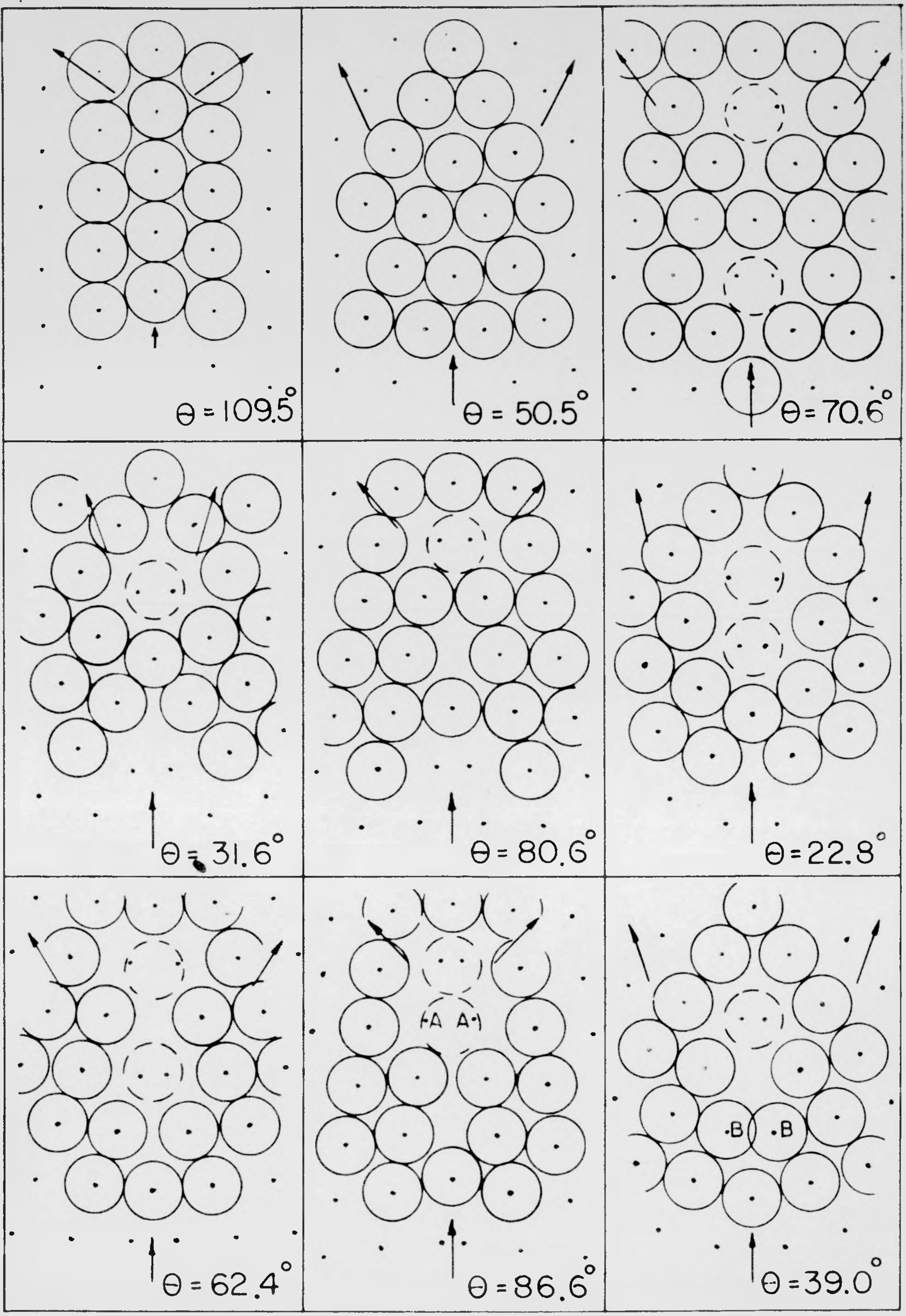

Fig. 3

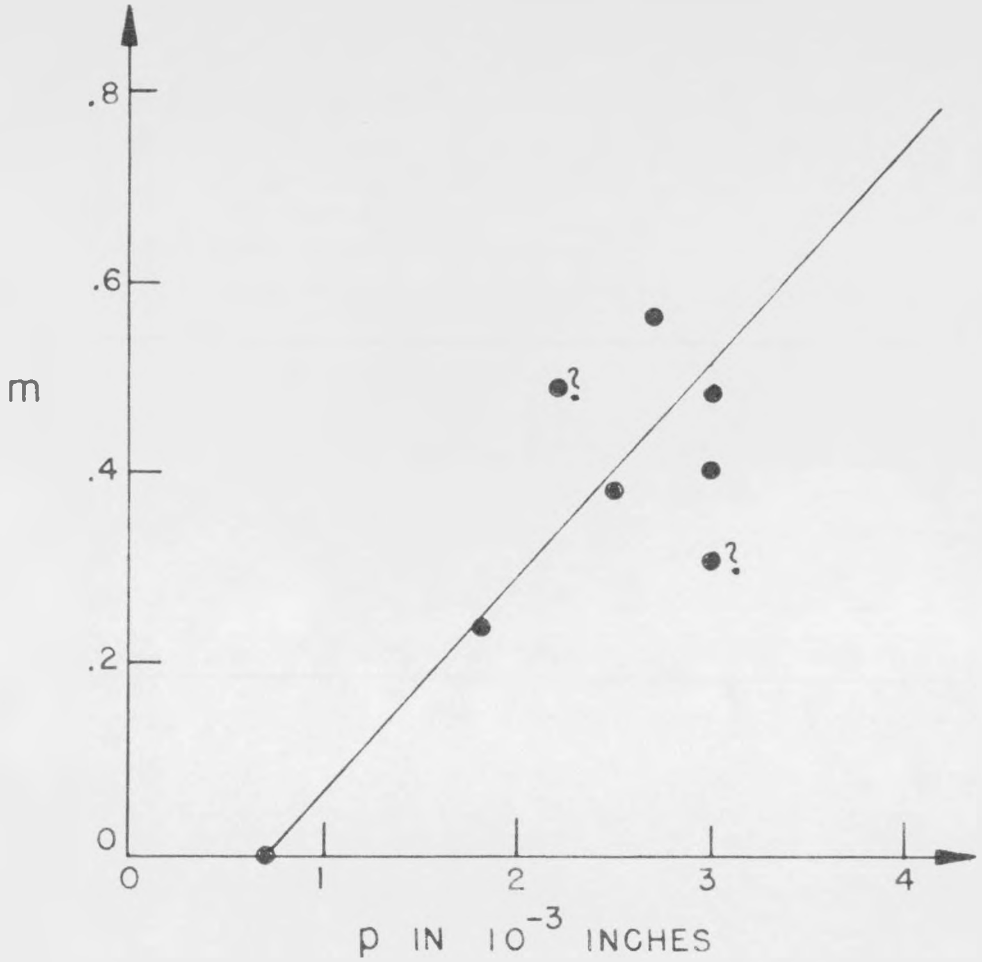

Fig. 4