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by Roy Ashley Smith, a candidate for the degree of M.S. in Metallurgical Engineering and find that in form and content it is worthy to submit to the examination committee.

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AN ELECTROLYTIC POLISHING AND RECRYSTALLIZATION STUDY OF ZINC AND ZINC ALLOYS

BY

Roy Ashley Smith

A

THESIS

sumbitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

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ABSTRACT

A Unitron hot stage and polarized light were used to enable direct observation of recrystallization in high purity (99.99 per cent) zinc and high zinc content alloys. Electrolytic polishing was investigated in an attempt to prepare unetched surfaces which would show good structural contrast under polarized light and thus permit structural changes occurring during recrystallization to be observed.

Kinetic data obtained from a sequence of photographs during each recrystallization trial showed typical sigmoidal isothermal reaction curves characteristic of a nucleation and growth process. It was determined that rates of nucleation and grain growth are a maximum over the same time interval that isothermal recrystallization rates show a maximum.

Grain growth rates were found to be irregular and to vary considerably for different grains of the same sample.

Orthophosphoric-ethyl alcohol solutions were the only electrolytes found which would give polished surfaces free of preferential attack at grain or twin boundaries. Operating voltages determined the contrast obtained when viewing the polished surface under polarized light. Current density was important in preventing etching and pitting.

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I. INTRODUCTION

Recrystallization studies on metals and alloys have been numerous for several years. Kinetic studies of the recrystallization process have been of great interest, both from a fundamental and practical aspect. Data concerning the rates of nucleation and grain growth as affected by fabrication, composition, and annealing temperatures are of immediate practical use to the fabricator interested in physical properties. This same data have been used to gain a more thorough knowledge of recrystallization mechanisms.

The problem undertaken in this investigation was to determine the feasibility of using a hot stage and polarized light to gain kinetic data for the recrystallization of zinc and high zinc content alloys. The anisotropic crystal structure of zinc permits orientation changes to be followed when viewed with polarized light.

When working with pure zinc or high zinc content alloys, the preparation of acceptable polished surfaces is extremely difficult. Mechanical polishing yields disturbed metal layers which give false indications of the true structure of the sample. Removal of the disturbed metal by etching is not feasible for two reasons:

1. Ample evidence has been accumulated by former researchers to establish that etched grain boundaries inhibit the free migration of newly formed grains during recrystallization.
2. Etching leaves films which make structural changes insensitive to polarized light.

Electrolytic polishing was used to avoid the above mentioned difficulties. In theory electrolytic polishing is ideal; however, in practice difficulties are numerous. A rather extensive study concerning the important variables in electrolytic polishing of zinc and zinc alloys was undertaken. In effect, this study made the thesis two fold, one part devoted to electrolytic polishing and the other part to the utilization of the polished surfaces for kinetic studies.

II. REVIEW OF THE LITERATURE

A. Introduction

Electrolytic polishing consists of the anodic dissolution of a sample under an applied potential in an electrolytic cell. Electrolytic polishing of metals gained stature when it was realized that mechanically prepared surfaces contained deformed and disturbed metal layers which did not represent true sample structure. At present, techniques have been devised to electrolytically polish many different metals, ranging from inactive metals such as gold to active metals such as magnesium. It can be stated that electrolytic polishing is predominantly an "art", not a "science"; hence, the skill and the experience of the operator is very important.

Since the purpose of this paper was not to study electrolytic polishing mechanisms, the literature review will not concern electrolytic polishing. "The Electrolytic and Chemical Polishing of Metals in Research and Industry", by Tegart[1] (1956) represents the most recent review and presentation of electrolytic polishing investigations.

Recrystallization concerns the formation of microscopically visible nuclei and their subsequent growth during the annealing of a cold worked material. The annealing of a cold worked metal or alloy is generally considered to involve three distinct processes: recovery, recrystallization, and grain growth. A fourth phenomenon termed "polygonization" has been noticed and studied extensively during the past fifteen years.

Recovery was originally defined as a change in the physical properties of a metal during annealing without any observable change in microstructure. X-Ray evidence has since shown definite structural changes to occur during periods of property change formerly associated with recovery. These structural changes have been termed "polygonization". As future evidence is gathered concerning the structural changes accompanying polygonization, it is entirely possible that the term "recovery" will be replaced by the more fundamental term "polygonization".

During recrystallization strain free nuclei form in the strained matrix, and grow by the consumption of surrounding cold worked material. The process is thus one of both nucleation and growth. The driving force for recrystallization is the residual energy of cold work in the deformed lattice. Recrystallization is complete when all the originally deformed material is consumed and replaced by new strain free grains.

Grain growth occurs after recrystallization is complete. An overall decrease in the number of grains will occur as larger grains absorb smaller ones. The driving force for this process is not the residual energy of cold work, but involves surface energy considerations.

This paper is concerned mainly with a kinetic study of recrystallization as followed by structural changes occurring on a free surface*. Therefore, this literature review will

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* The term "free surface", as used in this thesis, refers to the external surfaces created prior to, and persisting throughout, a given reaction as opposed to surfaces that might be created by sectioning during, or subsequent to completion of, the reaction.

mainly consider investigations related to this topic.

B. Isothermal Recrystallization in Terms of Nucleation and Growth

It was reasoned by Johnson and Mehl[2] (1939) that as in the case of eutectoid inversion and freezing, it should be possible to study the rate of isothermal recrystallization as a function of time, and it should also be possible to analyze the isothermal reaction curve into the component rates of nucleation and growth that determine them. Recrystallization was known at this time to involve nuclei formation and their subsequent growth as in the eutectoid solid solution decomposition.[3]

If kinetic studies were to shed much light on the recrystallization process a composite study involving the rate of nucleation, N, the rate of grain growth, G, and the corresponding isothermal recrystallization curve was needed. Stanley and Mehl[4] were the first investigators to undertake this problem. Previous measurements of N obtained by various investigators had generally shown N to increase with time, to be decreased by prior recovery, and to increase with increased deformation. Although some previous studies had shown G to decrease with time, most investigators had found G to remain constant with time.

Stanley and Mehl[4] used silicon ferrite (1 per cent Si) which had been rolled to 0.012 thickness, annealed, and extended 5 per cent. Samples were then annealed at 770°C for various times. Recrystallized grains reached sizes much larger than those grains in the surrounding cold worked matrix. Area measurements were made on the sheet surfaces and the number of recrystallized grains/cm^2, fraction recrystallized, and maximum grain size for each recrystallization time recorded. A plot of N vs. time gave a sigmoidal plot and showed N to increase with time, possibly passing through a maximum. A plot of the largest grain radius vs. time yielded a straight line and showed G to remain constant during recrystallization. Intersection of the straight line positively on the time axis suggested an "incubation period" was necessary for a grain to form. Other observations were that recrystallization yields isothermal reaction curves similar to other processes of nucleation and growth and that recovery preceding recrystallization decreases the rate of nucleation.

It should be noted that the data gathered by Stanley and Mehl was obtained from a free surface. The maximum grain diameters formed were larger than the sheet thickness. These particular conditions are referred to as "two dimensional recrystallization".

Anderson and Mehl[5] extended the work done by Stanley and Mehl to include the effect that the recrystallization variables of temperature, prior grain size, amount of deformation, and temperature had upon N and G in high purity aluminum. "Three dimensional recrystallization"* was also analyzed, whereby internal sections of aluminum sheet were observed after recrystallization. The effects of temperature were of particular importance in that the fundamentally important activation

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* In "three dimensional recrystallization" the thickness of the sheet is greater than the recrystallized grain size.

energies for N, G, and the composite recrystallization isotherm could be obtained. The results obtained by this extensive and "classic" recrystallization experiment are listed below:

1. Sigmoidal reaction kinetics are shown by nucleation and recrystallization isotherms.
2. G remains constant with time, increases with decreased grain size, increases with increased temperature, and appears to approach a maximum with increased deformation.
3. N increases with increased deformation, increased temperature, and decreased grain size.
4. The ratio N/G increases with deformation up to approximately 30 per cent extension. N/G decreases with decreased temperature.
5. Experimental variations of both N and G with temperature indicate that nucleation and growth in recrystallization are processes governed by activation energies.
6. Activation energies for N(Q_n) and G(Q_g) decrease with increasing deformation, the rate of decrease being greater for Q_n. Q_n and Q_g approach equal magnitudes with increasing deformation.
7. The time necessary for complete recrystallization in "two dimensional recrystallization" is roughly 1/3 that necessary for "three

dimensional recrystallization". G for "three dimensional recrystallization" was 1/3 that of "two dimensional recrystallization".

8. An incubation period seems necessary before nuclei form.
9. Recovery has no effect on N.

Considerable work was done to either confirm or disprove the findings of Anderson and Mehl. Suzuki[6] found G to decrease with time during recrystallization of high purity aluminum. Phillips and Phillips[7] found G to remain constant with time during recrystallization of heavily cold worked copper. They also noted that the ratio of the number of grains/cm^3 (calculated) to the number of grains/cm^2 was fairly constant for several purities of copper, regardless of the stage of recrystallization. Thus, the "planar" nucleation rate (grains/cm^2/sec) was directly proportional to the spatial nucleation rate (grains/cm^3/sec). Qualitative comparisons between the planar nucleation rates of two different materials should thus be valid.

Isothermal recrystallization curves have been constructed since the work of Anderson and Mehl[5] by using both microcalorimetric and microhardness data. Gordon[8] has employed both techniques. Cold worked specimens of copper were recrystallized at selected temperatures and the heat evolved with time measured. The heat evolved represented that portion of the energy expended in deformation which remained in the copper as residual energy of cold work. By plotting the fraction of the total heat evolved vs. time, sigmoidal isothermal recrystallization curves were obtained. Similar curves were obtained by statistically evaluating microhardness readings on samples which had been annealed at a given temperature for various times.

The work of Gordon[8] showed that approximately 1 per cent to 10 per cent of the energy expended in deformation was retained in the strained lattice and the greater portion of this energy was released during recrystallization. Some energy was also released during recovery. Gordon assumed that the energy released during recrystallization provided a "self sustaining" driving force in addition to the strain energy in the cold worked matrix.

C. Direct Observation of Recrystallization and Free Surface Considerations

Although the previously mentioned work firmly established recrystallization as a nucleation and growth process and provided information concerning the effects of different variables on N and G, direct observation of nuclei formation and growth had not been made. Brinson and Moore[9] directly observed recrystallization in zinc with a hot stage and polarized light. They found that new grains formed mainly at grain or twin boundaries where localized strain in the lattice was greatest. This knowledge in itself was not new.

The most interesting observation made was the irregular and intermittent nature of grain growth. Some nuclei had little capacity for growth and would remain stagnant. Other nuclei would show high initial rates of growth, remain dormant for a considerable length of time, and then resume growth.

In viewing the intermittent growth of nuclei, Brinson and Moore[9] found evidence contradicting the assumption of Anderson and Mehl[5] that a nucleus grows at a constant rate to the size necessary for observation. Brinson and Moore believed that the increase in N found by Anderson and Mehl was probably "apparent" and that the "true" rate of nucleation was either independent of, or even decreased slowly with time.

Brinson and Hargreaves[10] adapted a hot stage which would permit indentations to be made in selected sample areas during the direct observation of recrystallization in pure zinc. They found that nuclei could be stimulated by indentation, but that growth of these nuclei only occurred in regions where nuclei normally formed and grew: notably at grain boundaries and twinned regions. This was further evidence of the known facts that deformation is inhomogeneous and nuclei form and grow preferentially in areas of greatest dislocation density.

Several workers have questioned the authenticity of any rate measurements made on a free surface. Maddigan[4], in a discussion of Stanley and Mehl's measurements of N and G on a free surface, cited the fact that a surface represented a different state than an internal section. He also noted that an additional free energy interfacial term would be present and cited the work of Koehler[11] which indicated that dislocations tend to be drawn to a free surface. Anderson and Mehl[5], although finding N and G to be greater on the free surfaces of thin sheet (0.015 in) than on internal sections in thick sheet (0.125 in), suggested that varying degrees of preferred orientation between the two thicknesses might contribute to the differences measured. Prior work on single crystals of aluminum had shown N and G to be dependent upon the orientation of the crystal with respect to the direction of straining[12] and that G was dependent upon crystallographic direction[13].

Burke, in maintaining that "...grain growth is inhibited by a free surface"[14], cites the work of Beck; wherein, as a consequence of a transition from "three dimensional" to "two dimensional" growth, the maximum grain size attainable in annealed sheets was approximately equal to the sheet thickness[15]. On the other hand, Chaston[16] has shown that grain growth in high purity silver proceeds at the same rate at the surface as in the center of the material.

III. POLISHING OF ZINC AND ZINC ALLOYS

A. Introduction

The recrystallization portion of this experiment required smooth, unetched surfaces which did not have disturbed metal layers. Etched twin or grain boundaries should not be present as they would act as barriers to grain boundary migration. Disturbed metal layers on the polished surface should not be present as they would give a false indication of true sample structure.

Mechanical, chemical, and electrolytic polishing methods were used in an attempt to prepare polished surfaces meeting the above requirements. Although electrolytic polishing was the only technique which gave adequate surfaces, the work done using mechanical and chemical polishing will be presented. Listed below are the compositions of the materials polished:

Zinc Spelter: 99.99% by wt. Zn

Zinc base, copper alloy: 0.75% by wt. Cu, balance Zn

Zinc base, copper-titanium alloy: 0.3% by wt. Cu
0.3% by wt. Ti
balance Zn

Zinc base, magnesium-aluminum alloy: 0.075% by wt. Mg
0.9% by wt. Al
balance Zn

B. Mechanical Polishing

Mechanical polishing of the alloys was attempted after initial attempts at chemical and electrolytic polishing were unsuccessful. Mechanical polishing eliminates the problem of different dissolution rates of alloy phases during chemical or electrolytic polishing; however, the softness of high zinc content material promotes scratching and cold working of the sample during mechanical polishing.

Samples were cut and mounted in Nu Weld*. Conventional wet grinding through 600 grit, followed by polishing on a billiard cloth with Linde B abrasive was performed. Final polishing was done using a finishing cloth with Gamma #3 abrasive. The samples were then washed with water and dried quickly by a blast of air. This drying technique was the best found, as washing with alcohol prior to drying caused slight staining.

When the samples were microscopically examined under polarized light, grain structure and numerous small twins could be seen. Samples of the Zn-Mg-Al alloy were then electrolytically polished using different time intervals. Forty-five minutes of electrolytic polishing were required to completely remove the small twins, which had formed during the final polishing operation. It was concluded that mechanical polishing could not be used.

C. Chemical Polishing[1]

Chemical polishing involves the immersion of a sample into a polishing solution without the application of an externally applied potential. It is the absence of an external potential which distinguishes chemical polishing from electrolytic polishing.

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* Nu Weld is a plastic manufactured for denture purposes and requires no heat or pressure for setting. It is a product of the L. D. Caulk Company, Milford, Delaware.

Ideally, smoothing and brightening of the sample should occur without pitting or etching. Chemical polishing time will be shortened if it is preceded by careful mechanical polishing. Minimum polishing times are desirable as irregular removal of metal and/or etching may occur with extended polishing time.

Chemical polishing of zinc and the zinc alloys did not provide suitable surfaces, as both twin and grain boundaries were preferentially attacked. The Zn-Mg-Al and Zn-Cu-Ti alloys presented the additional problem of pitting due to preferential attack of intermetallic phases. No chemical polishing solutions were found which would enable an unetched surface to be prepared on pure zinc or zinc base alloys.

The following chemical polishing solutions were investigated and the results obtained with each are mentioned:

1. CrO_3-Na_2SO_4 Solution[17]

   This solution consisted of 160gm CrO_3, 20gm hydrated Na_2SO_4, and 500ml water. Preliminary cleaning of samples for 5 seconds in 50 per cent HCl preceded polishing. The samples were then dipped in the polishing solution for 20 seconds accompanied by vigorous agitation. Water was used to wash the samples and the polishing operation repeated until the desired polish was obtained. If brown films formed during polishing, a quick dip into a solution of 160gm CrO_3 per 500ml water was used as a wash.

   The CrO_3-Na_2SO_4 solution gave bright surfaces on pure zinc, but also attacked twin and grain boundaries.

No success was obtained in polishing the Zn-Cu, Zn-Mg-Al, or Zn-Cu-Ti alloys as brightening did not occur.

2. Nitric Acid Solution

The composition recommended by Tegart[1] was 75ml fuming nitric acid and 25ml water. Pitting and uneven removal of metal accompanied the polishing; therefore, this solution is not to be recommended.

3. CrO_3-Nitric Acid Solution

A saturated solution of CrO_3 in fuming nitric acid gave bright surfaces for the pure zinc and the alloys. This solution is to be recommended for polishing where grain size measurements are to be determined. Slight etching at twin and grain boundaries delineated structural features.

D. Electrolytic Polishing

Electrolytic polishing consists of the anodic dissolution of a sample in an electrolytic cell. A direct current power source is needed, which will permit various voltages to be applied to the cell. Although chemical and electrolytic polishing are similar in that dissolution of the sample occurs, greater control over dissolution rate is provided by the various potentials which can be applied to the sample in electrolytic polishing.

Two processes, brightening and the removal of surface irregularities, occur during electrolytic polishing. It is generally thought that brightening results from the formation of thin films on the metal surface. Evidence will later be presented which will verify that films definitely form on copper bearing zinc. The varying degrees of contrast observed, when using polarized light on surfaces of zinc which have been electrolytically polished under different conditions, indicate that films of variable thickness are present. It is also quite noticeable that electrolytically prepared surfaces are more resistant to scratching and to atmospheric attack than are mechanically prepared or etched surfaces.

Removal of surface irregularities during electrolytic polishing is attributed to a viscous layer of reaction products, which form during anodic dissolution and surround the sample. This layer protects the sample from direct chemical attack by the electrolyte. Presumably, surface elevations are not protected as much by the viscous layer as are grooves or depressions in the sample surface. Consequently, elevated areas go into solution at faster rates and a flat surface results.

During the electrolytic polishing of zinc in an orthophosphoric-ethyl alcohol electrolyte without mechanical stirring, the viscous layer is clearly visible and streams from the sample. If the layer is disturbed by swabbing or fast stirring, the sample immediately becomes dull. Hydrogen evolution accompanies this dulling and indicates that the sample is undergoing direct chemical attack by the electrolyte and is no longer protected by the viscous layer.

Several noticeable events occur when a sample of zinc is polished in an orthophosphoric-ethyl alcohol mixture.* During the first few seconds, the sample will become dull and hydrogen will evolve. This will be followed by a rapid brightening of the sample and the cessation of hydrogen evolution. An increase in voltage and a decrease in current will accompany brightening and the termination of hydrogen evolution. The viscous reaction product layer is forming and acts as protection to the sample from direct chemical attack by the electrolyte. Changes in the voltage and current show that the viscous layer has increased the resistance of the cell.

If the sample is removed from the cell shortly after it becomes bright, microscopic examination will reveal that grain boundaries and twin boundaries, if present, are slightly etched. A minimum polishing time is necessary to remove the etched remnants formed prior to the viscous layer. Increasing the voltage one or two volts above normal polishing values** when the sample is put into the electrolyte will enable the viscous layer to form more quickly and reduce the extent of the initial etching.

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* A potential should be applied to the cell prior to sample contact with the electrolyte.

** Normal polishing voltages will range from 1.5 to 4.5 volts depending upon the concentration of the orthophosphoric-ethyl alcohol solution and other polishing variables.

E. Variables Related to Electrolytic Polishing of Zinc and Zinc Alloys in Orthophosphoric-Ethyl Alcohol Solutions

Unetched polished surfaces were obtained only by electrolytic polishing using orthophosphoric-ethyl alcohol solutions. Two reasons probably explain the suitability of these solutions for zinc and zinc alloys: 1. Orthophosphoric acid is a weak acid and does not attack zinc as vigorously as do the more common acids. 2. Orthophosphoric acid has a high viscosity and enables a viscous layer of protective reaction products to easily form.

Pure ethyl alcohol must be used since denatured alcohol will not yield bright surfaces. Although 98 per cent orthophosphoric acid has been recommended in polishing references, it offered no advantages over the more easily obtained 85 per cent concentrations. Impurity level of the acid, however, was found to be important. The following purity of orthophosphoric acid gave the best results:

Volatile acids (as acetic)	0.001%
Chloride (Cl)	0.0003%
Nitrate (NO_3)	0.0005%
Alkali and other phosphates	0.20%
Reducing substances	Passes test
Arsenic (As)	0.0001%
Heavy Metals (Pb)	0.001%
Iron (Fe)	0.003%
Phosphorous or hypophosphorous acid	Passes test

Mol. wt.	98
Conforms to ACS Specs.	
Assay (min)	85-88% H_3PO_4

Several variables are of importance in electrolytic polishing. The frequent inability to reproduce previous results, when operating under what appeared to be identical conditions, indicated a complicated interdependence of variables. The following discussion will include observations of polishing variables which have been made while working with orthophosphoric-ethyl alcohol solutions. Although specific cells and their detailed operation will later be given, anyone engaged in electrolytic polishing should be aware of the probable effects to be expected by changing a given variable.

1. Electrolyte Concentration

An orthophosphoric-ethyl alcohol solution containing 37.5 per cent orthophosphoric acid was tried for polishing pure zinc.[1] Difficulties arose with this solution as a white film was present on the sample face after washing. Voltages of 4.3 to 4.5 volts were necessary to prevent etching and oxygen evolution on the sample frequently destroyed the polishing action. It was concluded that this solution did not contain sufficient acid content to permit the formation of an adequate protective viscous layer.

A 50 per cent orthophosphoric solution was tried for polishing pure zinc and found to prevent etching; however, the increased acid content caused pitting. After trying several different concentrations, it was found that 43.6 per cent orthophosphoric solution eliminated both etching and pitting of pure zinc.

From the above information and other work which was done, the following statements may be made concerning electrolyte concentrations.

a. Low acid concentrations favor etching while higher acid concentrations tend toward pitting. When acid concentrations as high as 70 per cent are reached, etching will occur.
b. Higher voltages may be applied using low acid concentrations without oxygen evolution at the anode.
c. Zinc alloys will generally require higher acid concentration for brightening than pure zinc.
d. Acid concentrations below 43.6 per cent orthophosphoric acid should not be used.

2. Voltage

A certain minimum voltage is necessary in order to prevent direct chemical attack of the sample and enable polishing to occur. The maximum possible voltage is that which can be used without oxygen evolution at the anode. These two facts are generally all that one will find regarding voltage when reading the literature on electrolytic polishing. However, when the polished sample is not to be etched after polishing and good contrast under polarized light is needed for photography, the lowest possible voltage which will prevent etching should be used.

The use of minimum voltage to get good contrast under polarized light cannot be overemphasized. Polished surfaces can be obtained using high voltages which appear better to the naked eye than surfaces obtained using lower voltages, but they will show poor contrast under polarized light. Figures 1 and 2 represent samples of cold worked zinc (partially recrystallized) which were polished in a 50 per cent orthophosphoric acid solution. Figure 1 sample was polished using 4 volts, while Figure 2 sample was polished using 2 volts. Superior contrast in Figure 2 is quite evident.

3. Current Density

It is the feeling of the author that initial attempts at electrolytic polishing should put more emphasis on voltage considerations than upon current density. When a voltage is found which works, the current density can be recorded and subsequent polishing performed using the appropriate values. A minimum current density will be found necessary in

Figure 1
Cold worked zinc (partially recrystallized) electrolytically polished in a 50 per cent orthophosphoric-50 per cent ethyl alcohol solution at 4 volts. Polarized light. 46.3x

Figure 2
Cold worked zinc (partially recrystallized) electrolytically polished in a 50 per cent orthophosphoric-50 per cent ethyl alcohol solution at 2 volts. Polarized light. 46.3x

order to obtain polishing without etching. This minimum value was found to be 0.16 amps/in^2 for a 50 per cent orthophosphoric-ethyl alcohol solution.

Increases in temperature, stirring rate, sample area, cathode area, and voltage all serve to increase current density. Increases in anode-cathode spacing decrease current density.

4. Stirring Rate

Stirring is an important variable and is necessary in electrolytic polishing. Circulation of the electrolyte prevents extreme "concentration polarization" in the cell. Polishing conditions vary with time when stirring is not used, as "concentration polarization" causes a continual decrease in current density and an increase in voltage. Depending upon the voltage reached, this trend is climaxed by oxygen evolution on the sample.

Stirring also removes bubbles which adhere to the surface being polished. The high viscosity of orthophosphoric acid causes bubbles to be trapped and retained in the electrolyte. Bubbles may originate from two sources: a. Hydrogen bubbles liberated at the cathode are dispersed throughout the electrolyte and can impinge on the sample. b. Localized cell action between the zinc matrix and intermetallic phases may cause displacement of hydrogen during the polishing of alloys. These hydrogen bubbles are minute and adhere tenaciously to the sample face. Regardless of their source, bubbles will always cause pitting when they remain on the sample being polished.

Although high stirring rates are desirable to remove bubbles, the following two considerations will govern the maximum agitation that can be used: a. Excessive agitation will destroy the protective viscous layer and cause etching. b. Striating or channeling of the sample will occur due to irregular flowage of the electrolyte over the sample face with excessive stirring. Magnetic stirring was found to best satisfy the above considerations.

An ideal polishing cell would permit stirring to be used for control over current density and voltage and would not necessitate stirring velocities to be determined solely by rates necessary to remove bubbles from the sample face. It is frequently easier to obtain small changes in current density and voltage by varying stirring rate than by changing the voltage applied to the cell.

5. Temperature

Prior to polishing the Zn-Mg-Al and Zn-Cu-Ti alloys, both of which have intermetallic phases, it was felt that lower polishing temperatures would tend to reduce direct chemical attack of these phases. Unfortunately, this assumption was in error for polishing trials at temperatures as low as 5°C did not reduce pitting at the grain boundaries, where the intermetallic phases were present.

The best polished surfaces were prepared with an electrolyte temperature of 32°C. Samples polished at temperatures lower than 32°C had poor contrast when viewed under polarized light. Evidence was obtained which indicated that the samples being polished reached a temperature greater than that of the electrolyte. Cold worked samples of zinc which were known to begin recrystallization at a minimum temperature of 43°C were polished and found to have partially recrystallized even though the maximum temperature of the electrolyte was only 32°C.

6. Sample Area

A small surface area of the sample should be in contact with the electrolyte in order to permit polishing at low voltages. Voltage increases must accompany any increases in areas to be polished. Excellent surfaces on pure zinc and the Zn-Mg-Al alloy were obtained with

0.22 in^2 of sample immersed and 2 volts applied to the cell. When the sample area was increased to 0.79 in^2 a minimum voltage of 3.75 was needed. As previously mentioned, low operating voltages gave samples having better contrast under polarized light.

Current density can be varied during polishing by raising or lowering the sample in the electrolyte. Although lowering the sample further into the electrolyte will cause a total current increase, this increase will not be proportional to the increase in sample area exposed to the electrolyte. The net result will be a decrease in current density.

7. Cathode Area

Tegart[1] mentions that large cathode areas should be used in order to insure more uniform polishing. No information was gathered to support or contradict this recommendation. It was noted that higher voltages could be used without oxygen evolution on the sample when small cathode areas were used.

Within limits, varying the cathode area can control the current density. Continual increasing of the cathode area during polishing will increase the current density until a substantial thickness of dissolution products surround the sample. When this occurs, the reaction product layer prevents further current increase.

8. Anode-Cathode Spacing

Large anode-cathode spacing permits operating under higher voltages without oxygen evolution on the anode or sample. This fact is of importance when a particular material must be polished using high voltage. Spacings ranging from 2.50 to 3.75 inches were found to be appropriate.

9. Polishing Time

A sufficient electrolytic polishing time must be used to remove all disturbed metal which was formed during the initial mechanical polishing. Polishing time will also depend upon current density as current density values give a direct measure of the amount of material removed per unit time.

Polishing times needed when operating under a given current density were determined by working with pure zinc which was fully annealed. During mechanical polishing, twins would form on the sample face. The sample was then electrolytically polished for various times in order to determine the time necessary to remove all twins. When this time was determined, an additional 15 minutes of polishing was used in order to insure complete removal of the disturbed metal.

Polishing times were generally in the range of 45 to 75 minutes.

If electrolytically polished samples are to be examined using high magnification, an effort should be made to reduce polishing time to a minimum as a certain degree of rounding may occur during polishing. Corners are rounded somewhat faster than the center of the sample face.

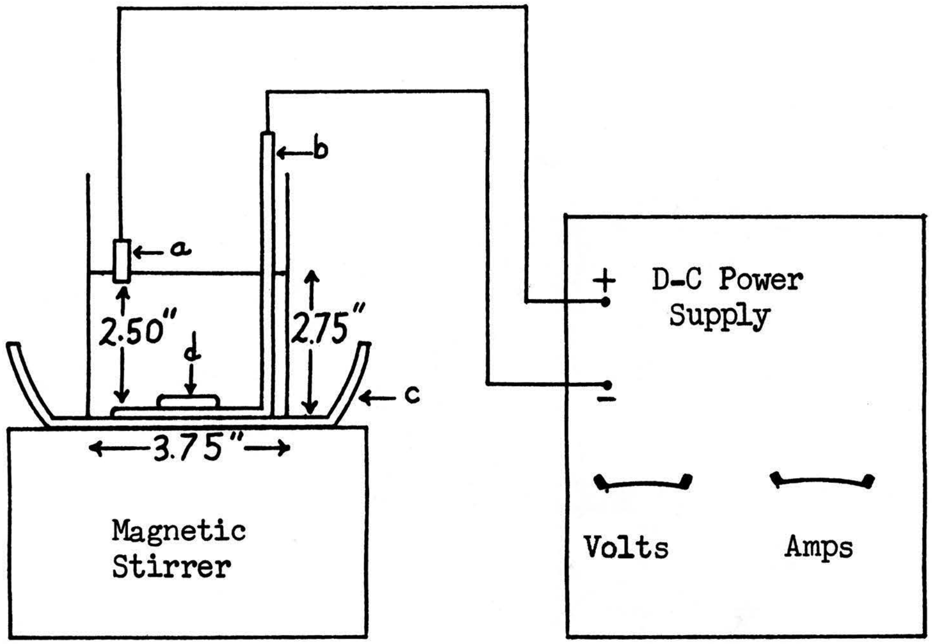
10. Sample History

While working with pure zinc and the Zn-Mg-Al alloy, it was noticed that annealed samples were much easier to polish than cold worked samples. Pitting and filming was more difficult to prevent when polishing cold worked material. These tendencies are apparently not peculiar to zinc and zinc alloys as Cortes[18] has noted varying degrees of difficulty when polishing refractory metals in the as cast, cold worked, and annealed conditions. It should be realized that sample history is an important variable in electrolytic polishing.

F. Recommended Electrolytic Cells for Orthophosphoric-Ethyl Alcohol Solutions

Figure 3 and Figure 4 show two different type of cell arrangements which were used. They are called "low voltage" and

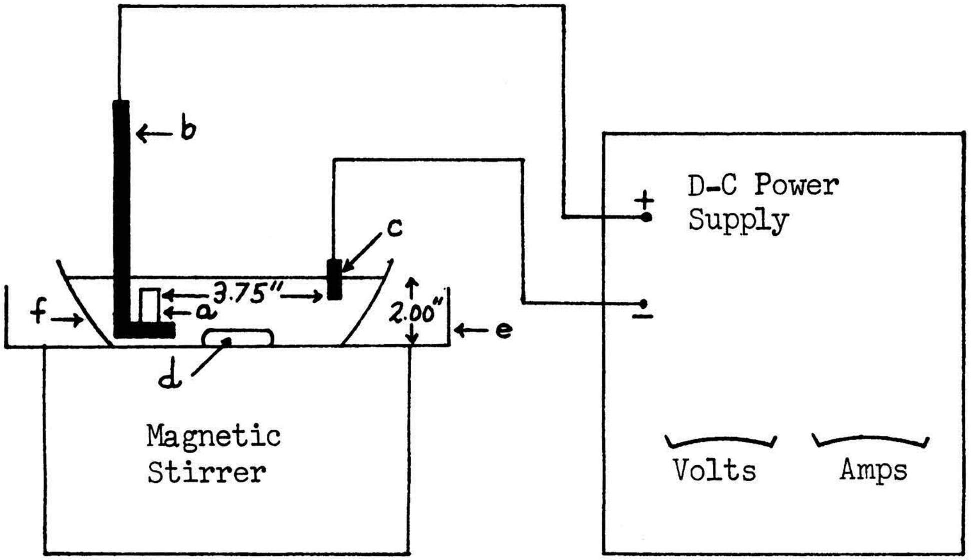
a. Sample (Anode)
b. Stainless steel cathode
c. Pyrex dish for temperature control with water
d. Magnet



<u>Operating Conditions</u>
Sample area immersed: 0.22 in^2
Current density: 0.16 amp/in^2
Voltage: 1.75 to 2.00 volts
Temperature: 32°C
Cathode Area: 14 in^2
Electrolyte: 50% Orthophosphoric acid-50 per cent ethyl alcohol

Figure 3
Low voltage cell and operating conditions.

a. Sample (Anode)
b. Stainless Steel sample holder
c. Stainless Steel cathode
d. Magnet
e. Aluminum pan for temperature control with water
f. Pyrex dish for electrolyte



<u>Operating Conditions</u>
Sample area immersed: 0.79 in^2
Distance of sample face below electrolyte level: 0.25 in
Current Density: 0.18 amp/in^2
Voltage: 3.75 to 4.05 volts
Temperature: 32°C
Cathode area: 1.5 in^2
Electrolyte: 43.6 per cent orthophosphoric acid-56.4 per cent ethyl alcohol

Figure 4
High voltage cell and operating conditions.

"high voltage" cells, respectively. Accompanying the figures are the operating conditions which should be followed for each cell. The low voltage cell gave the best results as good polished surfaces were obtained on pure zinc and the Zn-Mg-Al alloy. Listed below are the advantages and disadvantages to be expected with each cell.

1. Low voltage cell
    a. Advantages
        1. A small surface area can be used, which will enable a low operating voltage.
        2. Current density can easily be regulated by raising or lowering the sample.
    b. Disadvantages
        1. Bubbles rising from the cathode impinge on the sample face. Periodic swabbing should be used to remove bubbles not removed by stirring.
        2. Direct observation of the sample face being polished is difficult.
2. High voltage cell
    a. Advantages
        1. Bubble removal from the upright sample face is easier and is generally accomplished by the magnetic stirring alone.

2. The sample face being polished can be easily observed.
3. This cell can be used where high voltages are necessary.

b. Disadvantages

1. The high voltages required give polished surfaces which have poor contrast under polarized light.
2. Slight dissolution of the stainless steel sample holder contaminates the electrolyte.

A fine meshed material which would prevent cathode bubbles from contacting the sample face, yet not retard ion migration, would be an extremely useful addition to both cells. A material should be chosen which would not be attacked by the electrolyte. Fiberglass screen might be a suitable material as very fine meshes are available and no chemical attack by the electrolyte should occur. As previously mentioned, stirring rates would not be confined to high rates if bubbles could be prevented from contacting the sample face.

G. Electrolytic Polishing of Zinc Alloys in NaCNS Solutions

The following solution has been recommended for zinc alloys:[19]

200gm NaCNS
1000ml ethyl alcohol
100ml butyl cellosolve
20ml water

Although polishing was always accompanied by preferential attack of twin and grain boundaries, it is felt that NaCNS solutions offer promise for the polishing of zinc alloys. Less pitting and filming occurred using NaCNS solutions on Zn-Cu and Zn-Cu-Ti alloys than when orthophosphoric-ethyl alcohol mixtures were used. Operating conditions used for the above NaCNS solution were as follows:

Voltage: 20 to 25 volts
Cathode: Stainless steel
Anode-Cathode Spacing: 1/2 inch
Temperature: Approximately $20^{o}C$
Stirring Rate: Vigorous

Voltages of the above magnitude are needed to sustain brightening during polishing. Heating of the sample occurs and polishing time should be limited to 15 seconds, followed by sample cooling in water. Polishing times in excess of 15 seconds will cause pitting, staining, and irregular removal of metal. The sample should be held face down in the solution and a small surface area immersed.

During the first few seconds, a black film will form on the specimen. When the film starts flaking from the sample face, polishing begins. The sample should be manipulated by hand as the sample must be quickly removed from the solution after polishing and washed in water.

Several attempts were made to modify the composition of the NaCNS electrolyte. It was found that by reducing the NaCNS by one-half and adding NH_4OH lower voltages could be used and sample heating reduced. Reduction of operating temperatures was attempted, but results were inferior to those obtained when operating at room temperature. Further work should be done along the following lines:

1. Reduction of the NaCNS content and the addition of NH_4OH and other bases such as KOH should be tried.
2. Increased proportions of butyl cellosolve should be substituted for the ethyl alcohol.
3. Cathodes having a lower hydrogen overpotential than stainless steel should be tried in an attempt to reduce operating voltages without decreasing current density.

H. Film Formation in Zinc Alloys Containing Copper

Unexpected difficulties were encountered during electrolytic polishing of the Zn-Cu alloy which contained 0.75 per cent Cu. Since the copper is in solid solution it was assumed that pitting would not occur and the alloy could be easily polished: this assumption was true only in part. Bright surfaces without pits were obtained with the "high voltage" cell. However, when the sample was observed under polarized light during recrystallization in the hot stage, structural changes were masked by films.

Figure 5 shows a sample of the Zn-Cu alloy as it appeared under polarized light prior to recrystallization. Under normal (unpolarized) illumination the light areas showing twinned structures appear a light brown while the dark areas appear

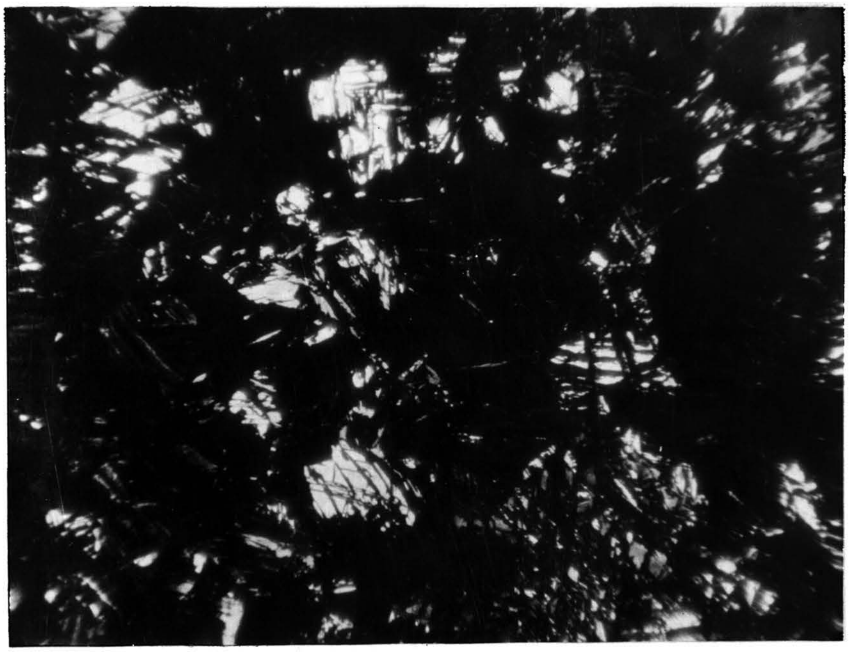


Figure 5
Cold worked Zn-Cu alloy electrolytically polished in high voltage cell. Polarized light. 46.3x.

Figure 6
Sample shown in Figure 5 after recrystallization in hot stage at 158°C. Polarized light. 46.3x.

bright. Rotation under polarized light causes sharp color changes to occur in the light areas, thus indicating that true structure is shown. Dark areas show only slight changes in color during rotation, thus indicating that films are partially masking structure.

Figure 6 shows the same sample after recrystallization in the hot stage at 158°C. Careful observation will show that some of the dark areas have changed to a lighter brown color. Light areas, however, have undergone no visible change. Figure 7 shows the same sample after removal from the hot stage and repolishing with the "high voltage" cell. It is clearly evident that the sample had recrystallized and that these changes had been masked by surface films.

Actually, two different type of films are represented by Figures 5 and 6. The light areas represent films which are inherently sensitive to polarized light. Color changes associated with these areas during roation are not caused by orientation changes of structure beneath the films. Films represented by the dark areas are not inherently sensitive to polarized light.

Numerous attempts were made to find electrolyte compositions which would eliminate film formation. NH_4OH was added to a NaCNS solution in an attempt to tie-up the copper in an ammonia complex. Figure 8 shows a color print from such an attempt. Included with the figure is the composition of the electrolyte used. The various blue colors suggest that a copper ammonia complex has been formed, but has adherred to the surface of the sample.

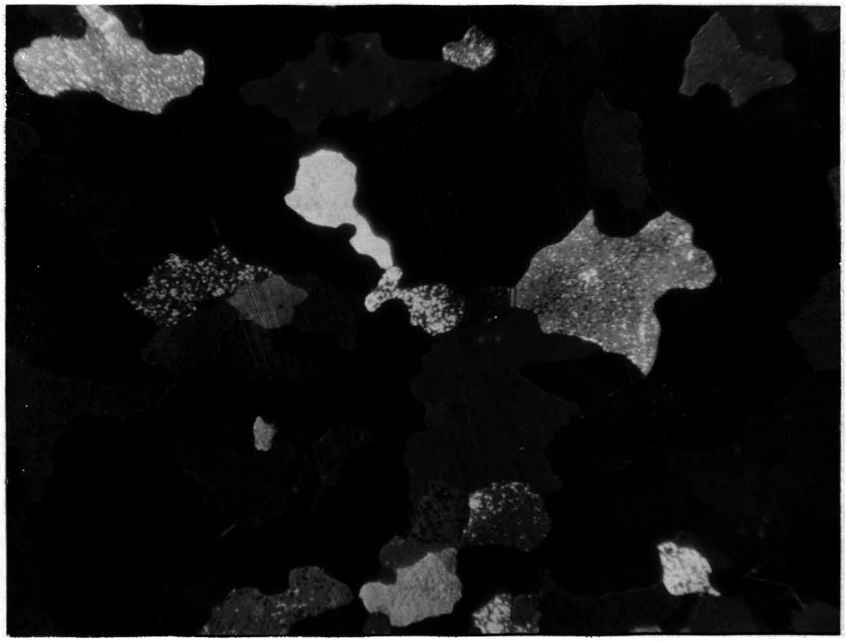


Figure 7
Sample shown in Figures 5 and 6 after removal from the hot stage and repolishing with high voltage cell. Polarized light. 46.3x

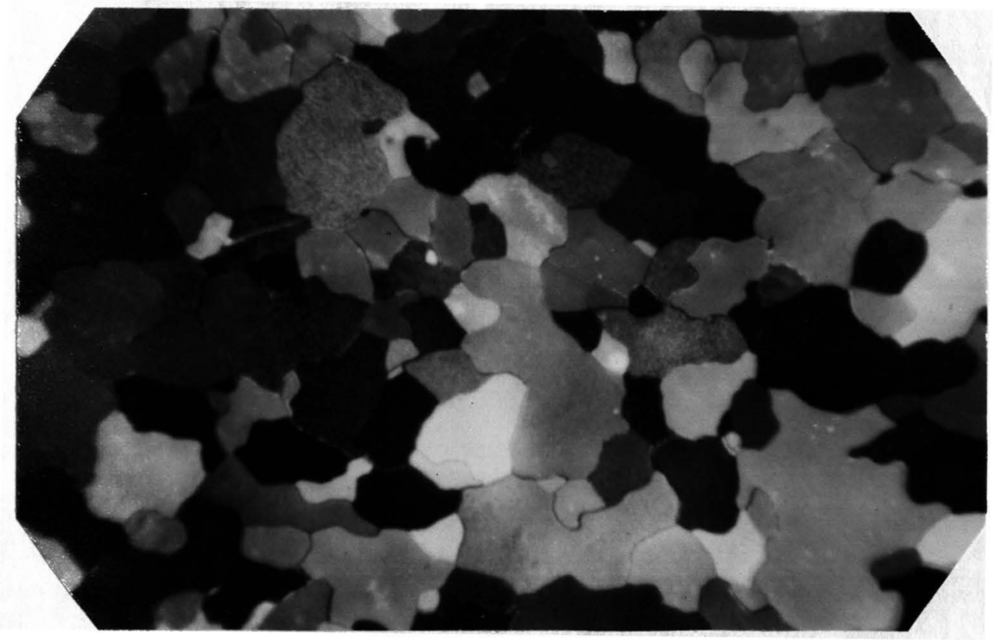


Figure 8
Colored print of electrolytically polished (see below) annealed Zn-Cu alloy. Polarized light. Approximately 50x

Electrolyte and Voltage Used
20gm NaCNS
10ml NH_4OH
125ml butyl cellosolve
125ml undenatured ethyl alcohol
5ml H_2O
10 volts

Future work is needed to solve the film problem encountered when electrolytically polishing zinc alloys containing copper. Two possible approaches are suggested below:

1. Polishing in Basic Solutions

   Basic solutions have been used for electrolytic polishing of zinc.[20] Thick, black layers form on Zn-Cu alloys upon contact with acidic solutions. This is evidence that lower pH values may favor the formation of copper compound films on the sample surface.

2. Electrolytic Plating of Copper from the Electrolyte

   It is possible that the copper going into solution during polishing could be plated from solution, if a cathode with a suitable potential were located near the sample face being polished. This would require an additional anode and cathode to be used in the electrolytic cell, with a power supply independent of that used for the regular anode and cathode.

I. Summation on Electrolytic Polishing Results for Pure Zinc and the Alloys

The low voltage cell gave surfaces for pure zinc and the Zn-Mg-Al alloy which were not etched, pitted, or filmed and had good contrast under polarized light. Suitable surfaces were obtained only for pure zinc and the Zn-Mg-Al alloy; consequently, the recrystallization portion of the thesis is devoted only to these two materials.

Although the Zn-Cu alloy could be polished in the high voltage cell without etching or pitting, filming occurred. Polishing in NaCNS solutions greatly reduced filming, but was always accompanied by preferential attack at grain and twin boundaries.

The Zn-Cu-Ti alloy was the most difficult to polish. No success was encountered in polishing the alloy in either the high voltage or low voltage cell. Although this alloy could be polished in NaCNS solutions, both etching and pitting at grain boundaries occurred.

IV. EXPERIMENTAL PROCEDURE

A. Casting and Fabrication

In order to eliminate the effect which grain size has upon recrystallization rate, a comparable grain size was needed for the zinc and the Zn-Mg-Al alloy. A grain size was needed which would be large enough to enable structural changes to easily be seen, yet small enough to include as many grains as possible in the field of view. Limited magnification was available as the highest power objective which could be used with the hot stage was 13.5x.*

Melting was done in graphite crucibles. Graphite molds were made by machining the mold cavity in 2 inch O. D. graphite rods. Split molds were not needed, as metal shrinkage during solidification enabled the casting to be removed.

The problems encountered with the pure zinc and the Zn-Mg-Al alloy were somewhat different. The Zn-Mg-Al alloy had a very fine grain structure upon solidification, and fabricating methods were needed which would not further refine the grain structure to the extent that it could not be resolved with low magnification; consequently, a minimum of hot rolling and a high rolling temperature were used. Large grains formed during solidification of the pure zinc and considerable rolling was needed to further refine the structure.

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* An adapter has now been obtained which will enable a Unitron 40x objective specially designed for use with a hot stage, to be used on a Bausch and Lomb Research Metallograph.

Figure 9 shows the Stanat Mill with the grooved rolls used to roll cylindrical shapes. Sizes larger than 0.600 inch in diameter had to be rolled on a larger rod mill.

Heating during the final cold working pass was sufficient to cause the zinc to recrystallize. As a result, the pure zinc was cooled to approximately 5°C in an ice water bath before final cold working. Upon exit from the rolls, the zinc also fell into an ice water bath. This same procedure was carried out for rolling of the Zn-Mg-Al alloy in order to eliminate the variable of deformation temperature.

Listed below are the procedures used for the pure zinc and the Zn-Mg-Al alloy:

1. Pure Zinc

    Cast at 540°C

    Casting dimensions, exclusive of riser: Diam., 0.850 in; Length, 4.00 in

    Homogenized at 350°C for 24 hours

    Hot rolled from 0.850 to 0.341 in diam. at 100°C

    Annealed 1 hour at 150°C

    Cold rolled to 0.305 in diam. (19.7 per cent reduction in area)

2. Zn-Mg-Al Alloy

    Cast at 570°C

    Casting dimensions, exclusive of riser: Diam., 0.625 in; Length, 3.75 in

    Homogenized at 350°C for 24 hours (homogenization at 375°C caused grain boundary melting)

Figure 9
Stanat Mill and grooved rolls.

Hot rolled from 0.625 to 0.341 in diam. at 250°C

Annealed 1 hr at 200°C

Cold rolled to 0.305 in diam. (19.7 per cent reduction in area)

It should be noted that raising the rolling temperature of the Zn-Mg-Al alloy was quite effective in preventing a decrease in grain size. Increasing the rolling temperature from 150°C to 250°C increased the grain size approximately one-third.

B. Operation of the Hot Stage

The Unitron hot stage is designed for use with a Unitron Metallograph. Unfortunately, the Unitron Metallograph did not provide sufficient light intensity for photographic purposes, when polarized light was used. As a result, the hot stage was used on a Bausch and Lomb Research Metallograph (Figure 10).

Figure 11 is an internal view of the hot stage chamber, showing the resistance heating element located in the upper half of the stage. Heat is conducted through the sample to the polished surface being viewed. Normally, the sample face is grooved for placement of the thermocouple, and a sample of sufficient length to extend upward into the cavity of the heating element is used. This practice was undesirable for zinc, as grooving of the sample face would cause cold working and possible recrystallization. Also it was found that temperatures were much higher in the heating element cavity than were recorded at the sample face; consequently, melting of the zinc could occur if long samples were used.

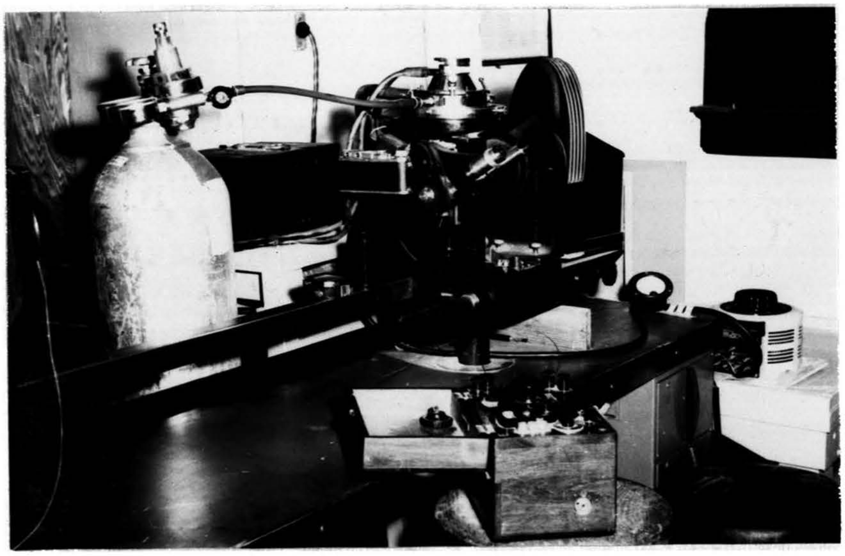

Figure 10
Experimental apparatus for recrystallization trials.

Figure 11
Internal view of hot stage..

To overcome the above difficulties, a copper sample holder was machined which would extend into the heating element and conduct heat to the sample (Figure 12). The base of the sample holder was grooved for placement of the iron-constantan thermocouple. High thermal gradients existed between the sample and the water cooled walls of the hot stage during heating. For this reason, the thermocouple junction had to be enclosed in a material extending into the heating element. The groove in the base of the sample holder provided the needed enclosure.

The following steps were performed for each recrystallization trial in the hot stage:

1. The polished sample was placed in the hot stage and the center of the sample selected for viewing.*
2. The sample was rotated under polarized light until the best possible structure contrast was obtained.
3. The hot stage chamber was evacuated and then flushed with argon. This procedure was repeated three times, followed by evacuation and the application of a static argon atmosphere at 33 psi.
4. Water was circulated through the hot stage at the rate of 0.5 liters/minute.
5. The sample was photographed. All changes that occur during recrystallization were noted by

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* During rolling, deformation is not uniform throughout the entire cross section. Since a comparison was desired between the zinc and Zn-Mg-Al recrystallization kinetics with identical cold work, focusing at different positions on the sample face would add an undesirable variable.

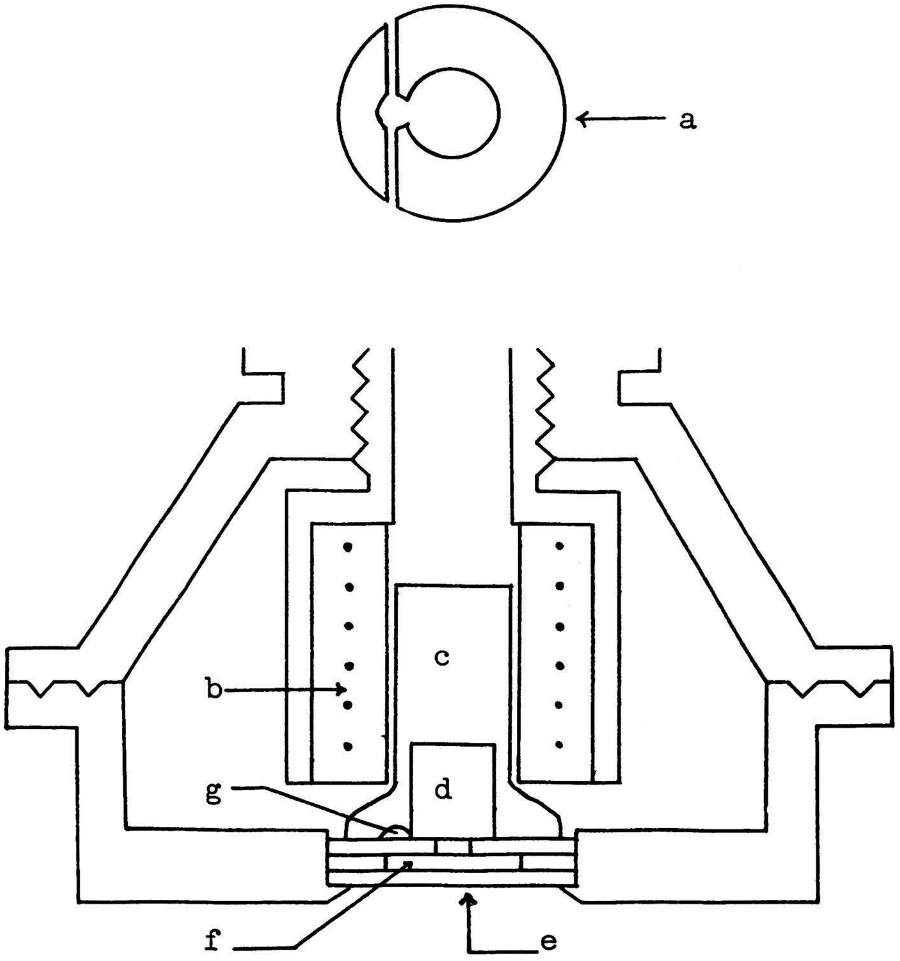


Figure 12
Arrangement of sample and sample holder in the hot stage.

a. Bottom view of sample holder showing groove for thermocouple placement
b. Resistance heating element
c. Sample holder
d. Sample
e. Quartz window
f. Quartz shutter, closed position
g. Thermocouple junction position

comparison with the first picture taken; therefore, it was imperative that the metallograph not be jarred after this first picture was taken as the sample may move.

6. Heating was started with an initial current of 4 amps, followed by increasing the current by one amp at two minute intervals until the desired temperature was reached.
7. Photographs were taken at selected intervals during recrystallization. A photograph was taken when the first change was noted and the time recorded as time "zero". If recrystallization was not complete after an appropriate length of time at the annealing temperature, the temperature was raised until the sample completely recrystallized and a final photograph was taken.

Several difficulties were encountered when performing the above steps. The following discussion concerns the problems of focusing, temperature control, and sample vaporization.

1. Focusing

   An adapter was made which enabled the 35mm camera to be attached at the bellows connection on the Bausch and Lomb Metallograph. Focusing was accomplished by using a magnifying eyepiece positioned over the focusing mirror of the 35mm camera attachment. Focusing by this method was difficult and time consuming. This focus was not the same as the focus needed when viewing the sample through the observation eyepiece of the metallograph. When observation of the sample indicated sufficient change had occurred to warrant a picture, the time necessary to refocus through the magnifying eyepiece was too long. This problem was remedied by recording the value on the fine focusing knob which corresponded to the focus needed for picture taking. When a picture was needed, the fine focusing knob could quickly be turned to the appropriate value and a picture taken immediately.

Thermal expansion during heating caused a change in focus with increasing temperature. For this reason, constant refocusing was needed until the desired reaction temperature was reached.

2. Temperature Control

Temperature control was maintained by a variable transformer. Fluctuations in the line voltage necessitated constant adjustment of the variable transformer in order to maintain constant temperature. Temperature control alone, required the entire attention of one individual. For this reason, an assistant was necessary when making a run.

3. Sample Vaporization

The first traces of sample vaporization were noted when pure zinc was annealed at 85°C. Vaporization was considerable when annealing the Zn-Mg-Al alloy at 162°C, as fogging of the quartz window prevented sample observation after one hour (Figure 12). In order to reduce the problem of fogging the quartz shutter was closed when a picture was not being taken or the sample was not being observed through the observation eyepiece. Cleaning of the quartz window was also performed after each run.

C. Photographic Procedure

Electrolytically prepared surfaces do not show high contrast between structural features when viewed with polarized light. A high contrast film is thus needed. A fast film was also needed in this investigation in order to take several exposures in a short period of time.

Panchromatic-X 35mm film was used and found to give a very thin negative, even with exposure times of 30 seconds. Tri-X Pan, a faster and a higher contrast film, worked much better and did not cause noticeable graining which is frequently observed in a fast film. From the standpoint of speed, a one second exposure using Tri-X Pan was approximately equivalent to a six second exposure using Panchromatic-X film.

A high contrast printing paper was needed to bring out the best possible contrast when making prints from the thin negatives. F-4 Kodabromide printing paper gave the best contrast prints. F-5 printing paper was tried and although higher contrast was obtained, delineation of structure was poor.

It should be noted that good contrast under polarized light is more easily obtained when using a low power objective. When high power objectives are used many of the shades obtained using low power objectives are no longer noticeable.

D. Interpretation of Photographs

All calculations were made by using the sequence of photographs taken during each recrystallization trial. Each photograph had an area of 100cm^2, while all samples had a polished surface area of 0.472cm^2. Photograph magnifications were 46.3x and 55.4x for the pure zinc and Zn-Mg-Al alloy respectively; consequently, 100cm^2 of photograph area represented 0.047cm^2 (9.9 per cent of the total area) of the zinc sample areas and 0.032cm^2 (6.7 per cent of the total area) of the Zn-Mg-Al sample areas.

A planimeter was used to calculate areas on the photographs which represented recrystallized grains. The first photograph taken prior to recrystallization and the last photograph taken after recrystallization was complete were used to determine recrystallized areas. Approximately twenty photographs were taken during each run, the majority being taken during the first stages of recrystallization when changes occurred rapidly.

V. EXPERIMENTAL RESULTS

A. Pure Zinc

Figure 13 shows four isothermal recrystallization curves for pure zinc. Typical sigmoidal curves characteristic of a nucleation and growth process are shown for the 65°C, 70°C, and 76°C runs; whereby, the reaction rate is initially slow, goes through a maximum in a linear fashion, and then decreases. The temperature for the 85°C run was high enough to eliminate the initial slow reaction rate present in the other three curves.

As seen in Figure 13, three of the curves show some recrystallization at time "zero". This is due mainly to recrystallization which occurred prior to heating in the hot stage. The ice water quench used during fabrication of the zinc had not been totally effective in preventing recrystallization. The following table includes per cent recrystallization prior to heating in the hot stage, temperature at which recrystallization was first observed, and the slope (k) of the linear portion of each reaction isotherm.

Recrystallization Temperature (°C)	Per Cent Recrystallization Prior to Annealing in the Hot Stage	Temperature of First Observed Recrystallization	k
65	2.9	43	0.007
70	5.7	55	0.025
76	0.2	52	0.089
85	2.0	74	0.101

Variations in the temperature of first observed recrystallization are probably the result of observation limitations. Samples were observed at 340x when attempting to note the first structural change occurring. It is entirely possible that areas not in the

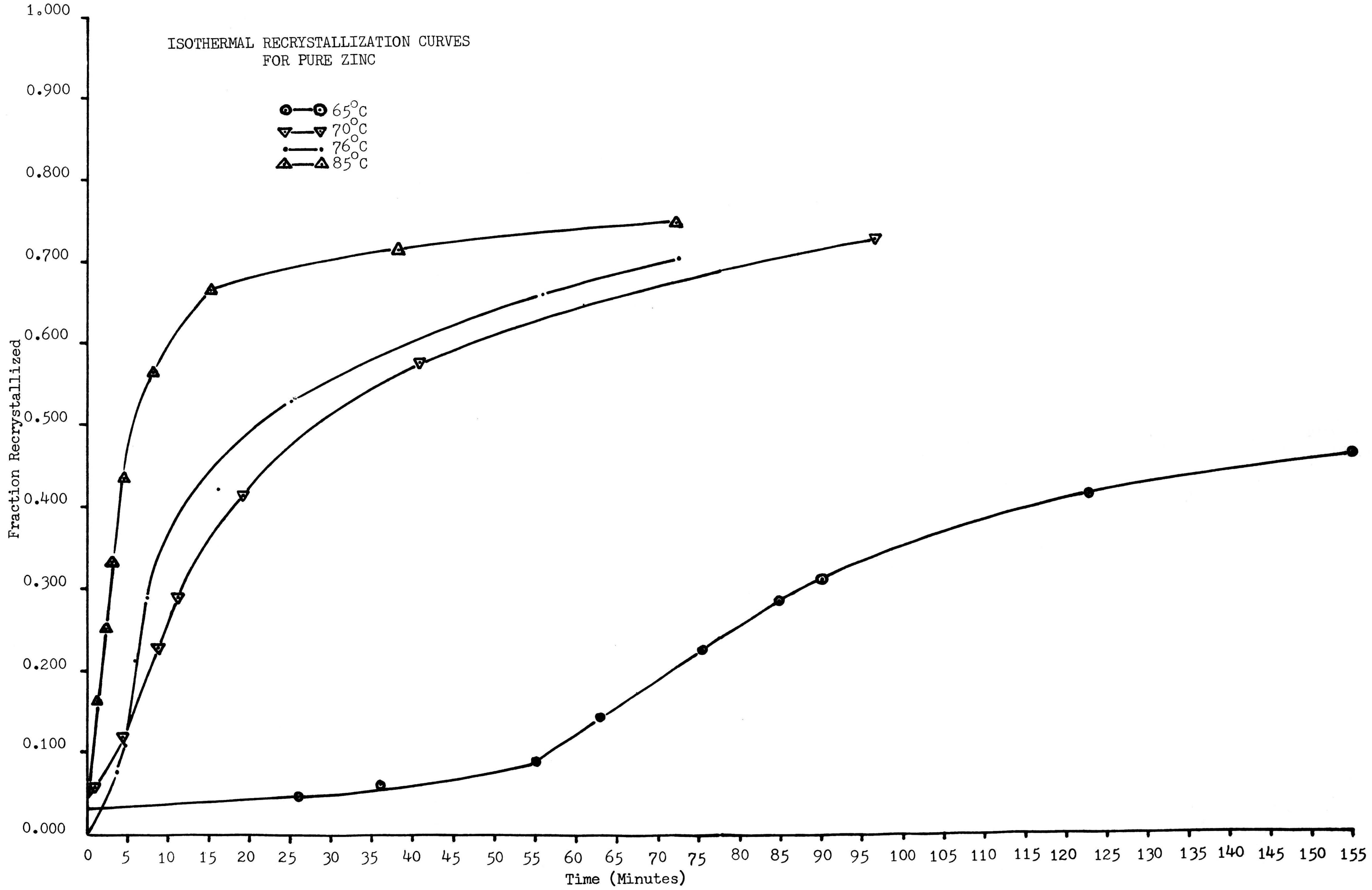

ISOTHERMAL RECRYSTALLIZATION CURVES
FOR PURE ZINC
65°C
70°C
76°C
85°C
Fraction Recrystallized
1.000
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
145
150
155
Time (Minutes)

Figure 13

field of view recrystallized at temperatures lower than those listed above.

The considerable difference shown in the initial recrystallization temperature of the 65°C and 85°C runs is due in large part to the rate at which the hot stage was heated, the rate being greater for the 85°C run. Slow heating rates always resulted in ititial recrystallization temperatures lower than those obtained with high heating rates. This observation is in agreement with the accepted fact that an incubation period is necessary before a recrystallized grain will form.

Figure 14 is an Arrhenius plot utilizing the "k" values to determine the activation energy, "E", for recrystallization of pure zinc. The slope of the straight line is -6350. Calculation of "E" is shown below:

$$\text{Slope} = \frac{-E}{2.30\ R}$$

$$E = -(-6350)(2.30)(1.99)$$

$$E = +29\text{kcal}$$

Limitations in the experimental procedure need to be mentioned in regard to Figure 14. The high thermal inertia of the hot stage prevented rapid heating to the desired reaction temperatures, and some recrystallization occurred in each run before the intended temperature was reached; consequently, "true" isotherms were not obtained and several temperatures were represented on the straight line portions of the isothermal recrystallization curves from which "k" values were determined. Points were plotted on Figure 14 for all temperatures falling on the straight line portion of each recrystallization isotherm.

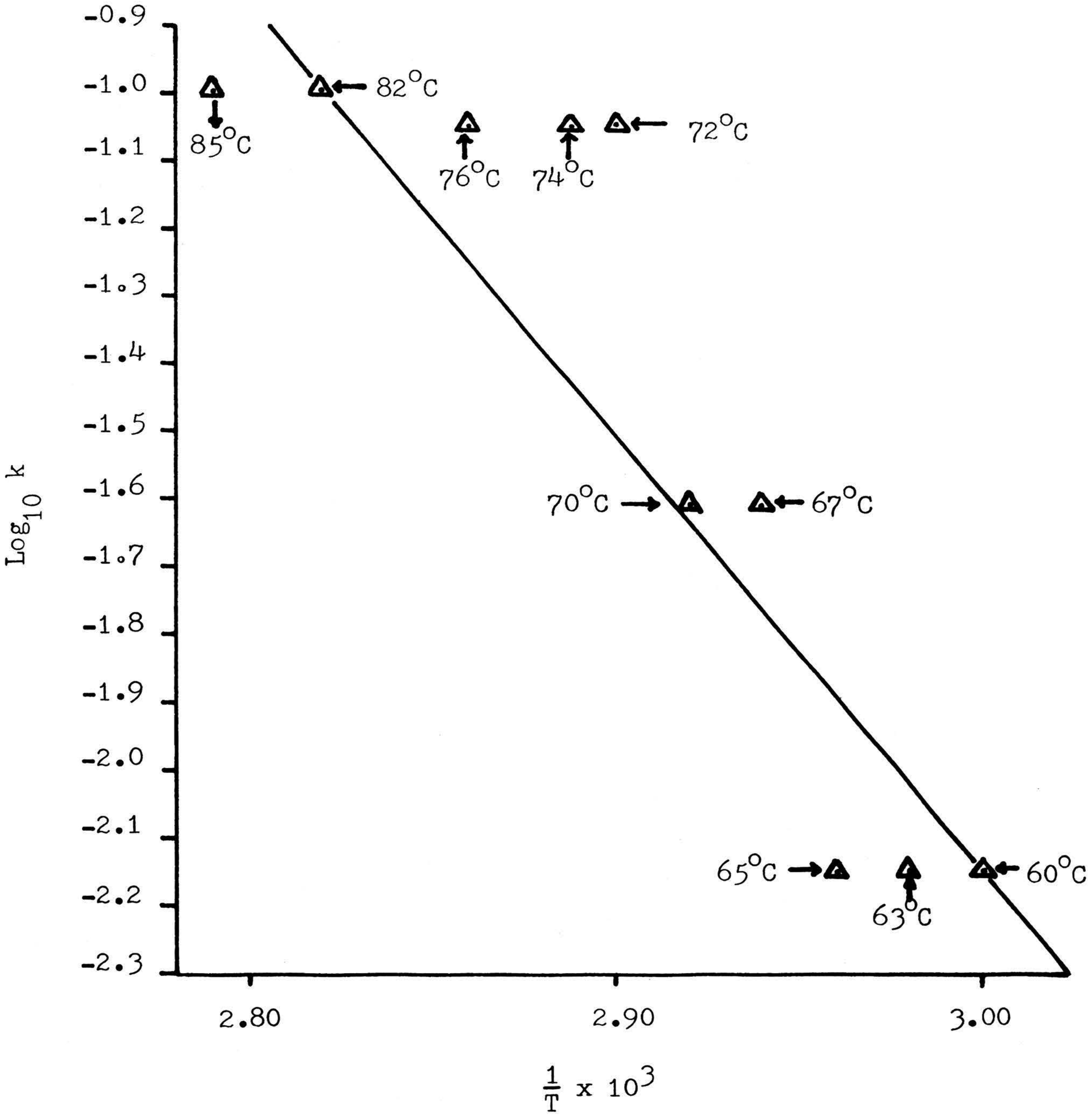


Figure 14
Variation of recrystallization rate of pure zinc with temperature.

For example, the linear portion of the 65°C recrystallization curve (Figure 13) for zinc contains points representing three different temperatures: namely, 60°C, 63°C, and 65°C. The log k value for the 65°C recrystallization curve is -2.15. Figure 14 thus shows $\frac{1}{T} \times 10^3$ values for 60°C, 63°C, and 65°C, all of which correspond to a log k value of -2.15.

It was noted that the first temperature falling on the linear portion of each recrystallization isotherm seemed to govern the maximum rate achieved. Subsequent higher temperatures did not cause an increase in the slope.

Ideally, greater temperature ranges should be used when determining activation energies. Since heating in the hot stage was slow, wide temperature ranges could not be used. As a result, an expanded temperature scale had to be used in Figure 14, which indicates a degree of accuracy not actually achieved.

As shown in Figure 14 the log k value for the 76°C run is nearly the same as that for the 85°C run, indicating that the rate for the 76°C run was abnormally high in comparison with both the 85°C and 70°C trials. The small amount of recrystallization prior to annealing in the hot stage, probably explains the high reaction rate obtained. If the other three samples had recrystallized an equal amount during fabrication the calculated activation energy would probably have been smaller.

The 65°C run was selected in an attempt to gather data concerning nuclei formation and their subsequent growth during recrystallization. Figure 15 is a nucleation curve obtained by counting the number of recrystallized grains visible in the field of view at various times. The nucleation curve shows a

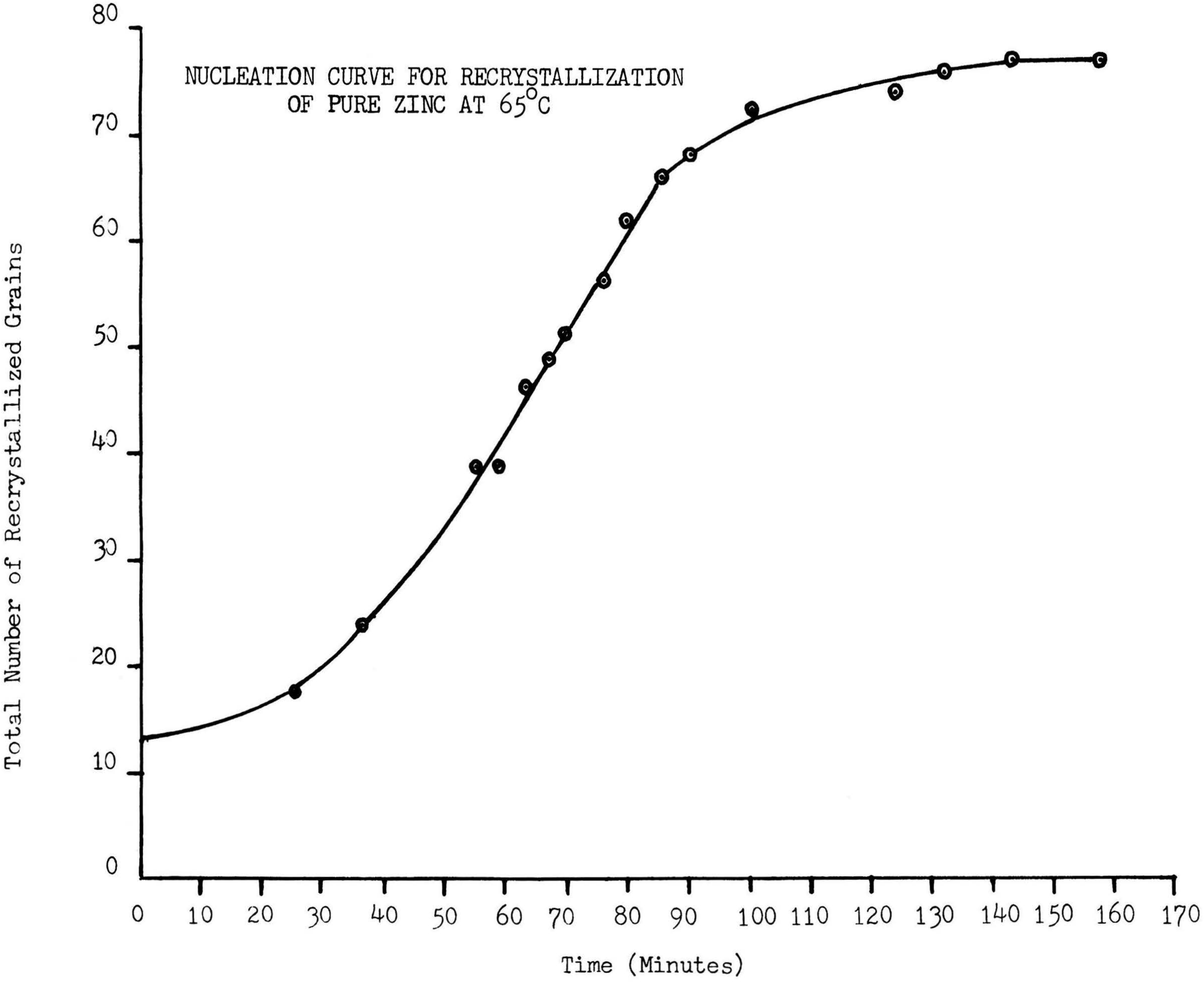

NUCLEATION CURVE FOR RECRYSTALLIZATION OF PURE ZINC AT 65°C
Total Number of Recrystallized Grains
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
Time (Minutes)

Figure 15

a sigmoidal shape similar to the isothermal recrystallization curves. The nucleation curve is also linear over the same time interval (55 to 85 minutes) as the corresponding 65°C isothermal recrystallization curve.

Figure 16 shows the nature of grain growth during recrystallization. Grains were chosen which were not in contact with other recrystallized grains and could thus grow freely in all directions on the surface being observed. As indicated, grain growth is highly irregular with time; however, the greatest growth rate for each grain occurs during the same time interval (55 to 85 minutes) that the isothermal recrystallization rate is the greatest.

Figure 17 is a sequence of photographs taken during recrystallization in the 85°C run. Careful comparison between photograph "a" and photograph "b" will reveal that several recrystallized grains present in the latter have small counterparts in photograph "a". These small counterparts represent recrystallization grains which formed prior to annealing in the hot stage. Such a comparison was used to determine the per cent recrystallization which had occurred prior to annealing in the hot stage.

It is evident that large grains recrystallize slower than small grains. All recrystallization trials showed this tendency. Large grains, which had deformed in a manner yielding broad twin bands of one orientation, showed a special tendency toward stability during annealing. The dark twin bands in the central portion of photograph "e" represent one of these stable grains.

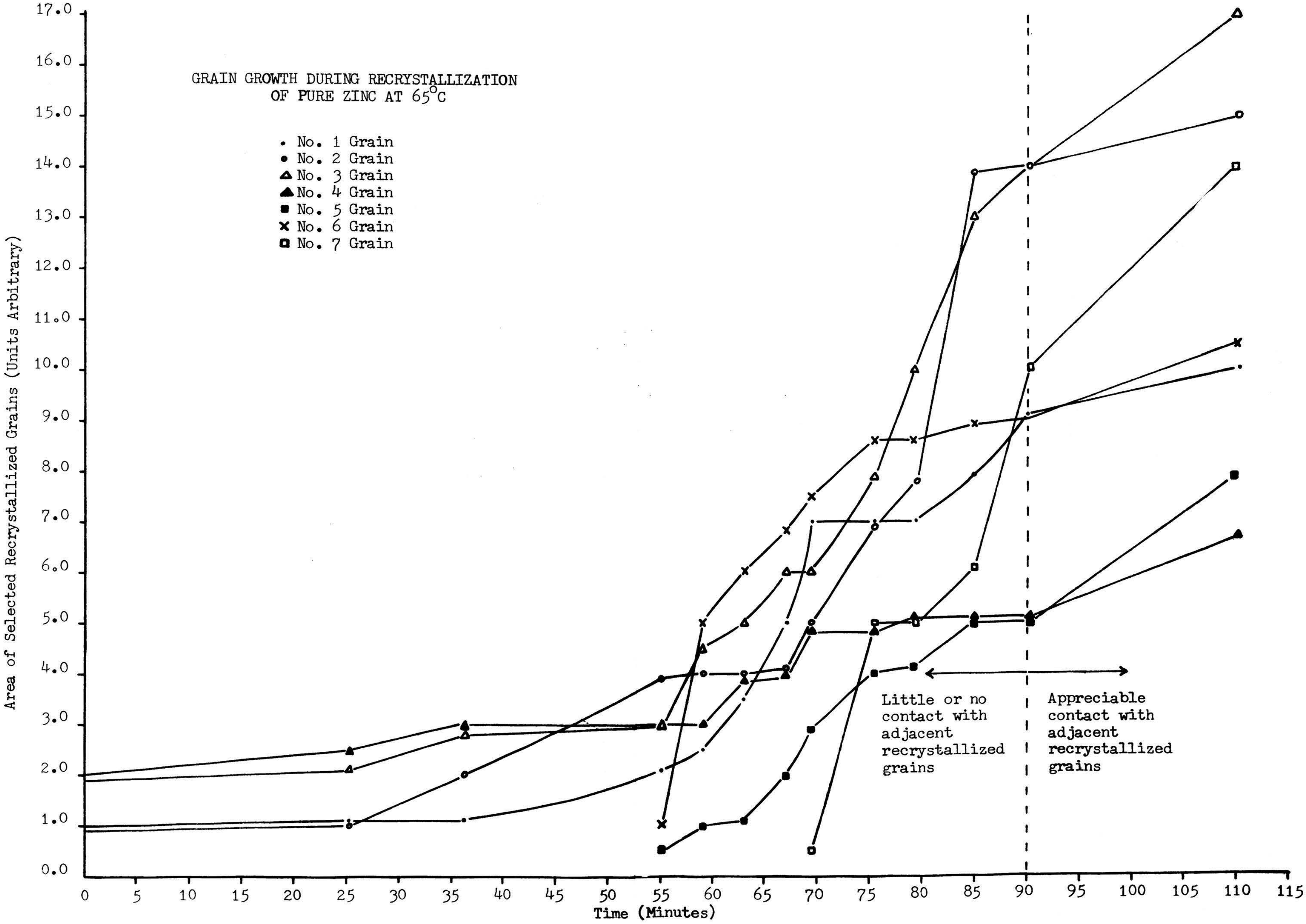

GRAIN GROWTH DURING RECRYSTALLIZATION OF PURE ZINC AT 65°C
· No. 1 Grain
● No. 2 Grain
△ No. 3 Grain
▲ No. 4 Grain
■ No. 5 Grain
× No. 6 Grain
▫ No. 7 Grain
Area of Selected Recrystallized Grains (Units Arbitrary)
17.0
16.0
15.0
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
115
Time (Minutes)
Little or no contact with adjacent recrystallized grains
Appreciable contact with adjacent recrystallized grains

Figure 16

a. Prior to heating in hot stage.

c. 3.23 minutes

e. 11.23 minutes

b. 2.67 minutes

d. 4.73 minutes

f. 39.15 minutes

Figure 17
Sequence of selected photographs during the recrystallization of pure zinc at 85°C. Time elapsed since the beginning of recrystallization shown for each photograph. Polarized light. 46.3x

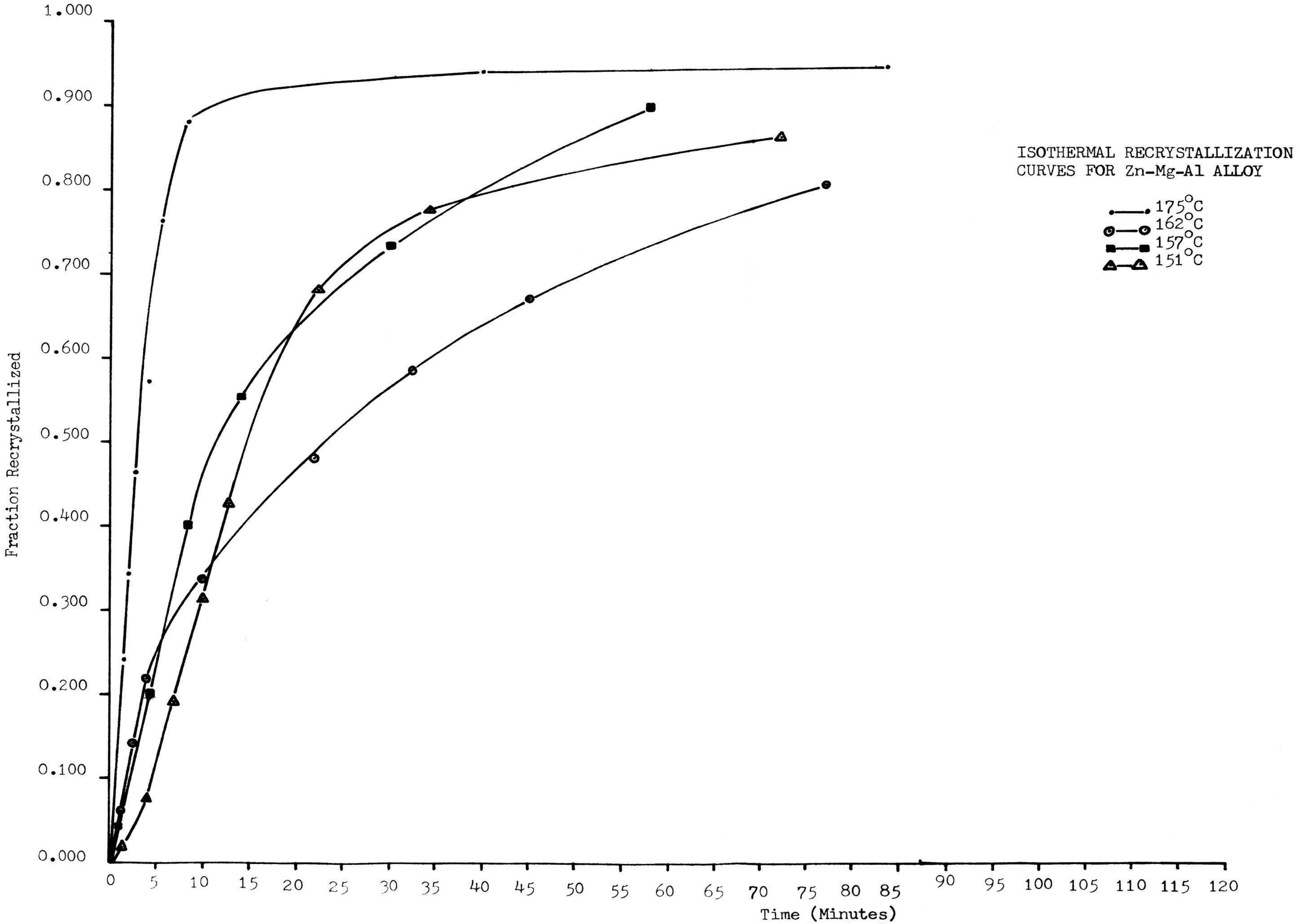
B. Zn-Mg-Al Alloy

Figure 18 shows the isothermal recrystallization curves obtained. The following table includes the slope (k) of each curve and the temperature at which recrystallization was first observed:

Annealing Temperature (°C)	Temperature of First Observed Recrystallization (°C)	k
151	150	0,041
157	153	0.048
162	150 to 155	0.057
175	158	0.168

Although the isothermal recrystallization curves are similar in shape to those obtained for pure zinc, several differences are present. All of the Zn-Mg-Al curves show no recrystallization at time "zero" as recrystallization had not occurred prior to annealing in the hot stage. Zn-Mg-Al reaction rates tend to be faster than those for pure zinc and the linear portions of each curve extend over a greater range before leveling off. Although a considerably higher temperature is needed to start recrystallization in the Zn-Mg-Al alloy, once this temperature is reached, reaction rates are greater than those for zinc.

Increased temperature has increased the slope of the straight line portion of each Zn-Mg-Al recrystallization curve; however, intersection of the curves occur when the reaction rate is no longer linear with time. The 162°C curve has a very short linear portion and does not recrystallize as much as the two lower



ISOTHERMAL RECRYSTALLIZATION CURVES FOR Zn-Mg-Al ALLOY
175°C
162°C
157°C
151°C
Fraction Recrystallized
1.000
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
115
120
Time (Minutes)

Figure 18

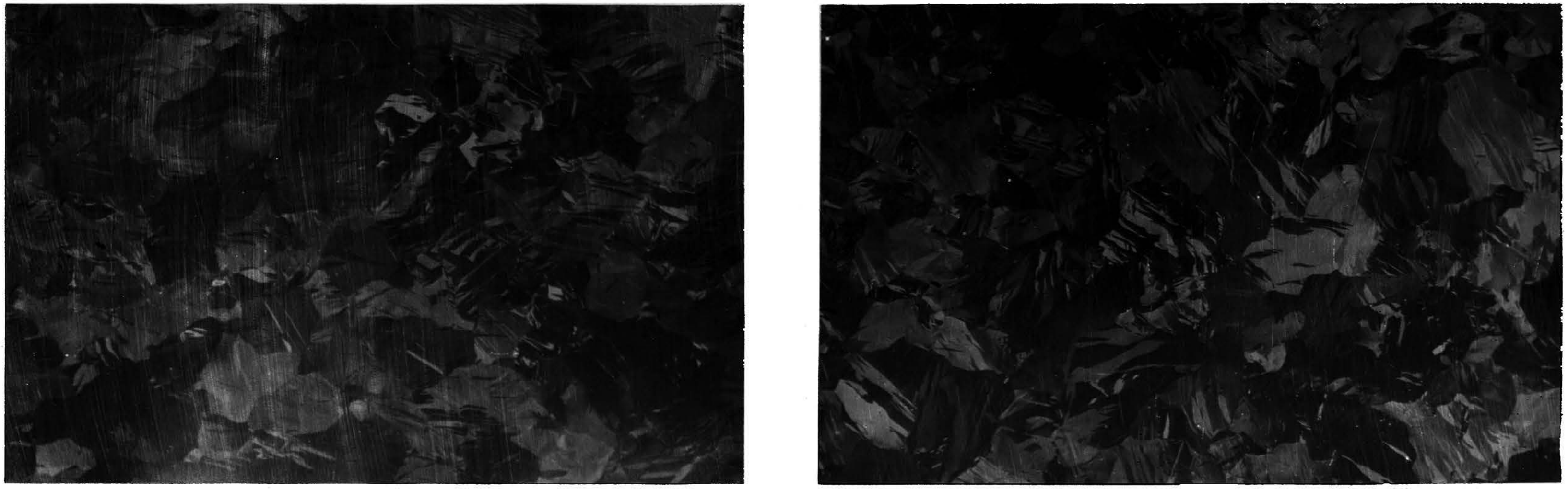
temperature curves. A short segment of the 151°C curve also shows a greater fraction recrystallized than the 157°C curve.

A comparison between the photographs for the Zn-Mg-Al trials showed that a uniform grain size had not been obtained. Figure 19 shows the cold worked structure prior to recrystallization in the hot stage and the structure after complete recrystallization for both the 151°C and 162°C runs. In comparing the cold worked structures it is quite evident that the 151°C sample has a finer and more uniform grain size than the 162°C sample. The recrystallized grain size of the 151°C sample is also more uniform than the recrystallized grain size of the 162°C sample.

The non-uniform grain size obtained was caused by a limited amount of rolling of the cast structure and the high rolling temperature (250°C) used. As previously mentioned, this practice was necessary in order to prevent a fine grain size, which could not be resolved with the limited magnification available.

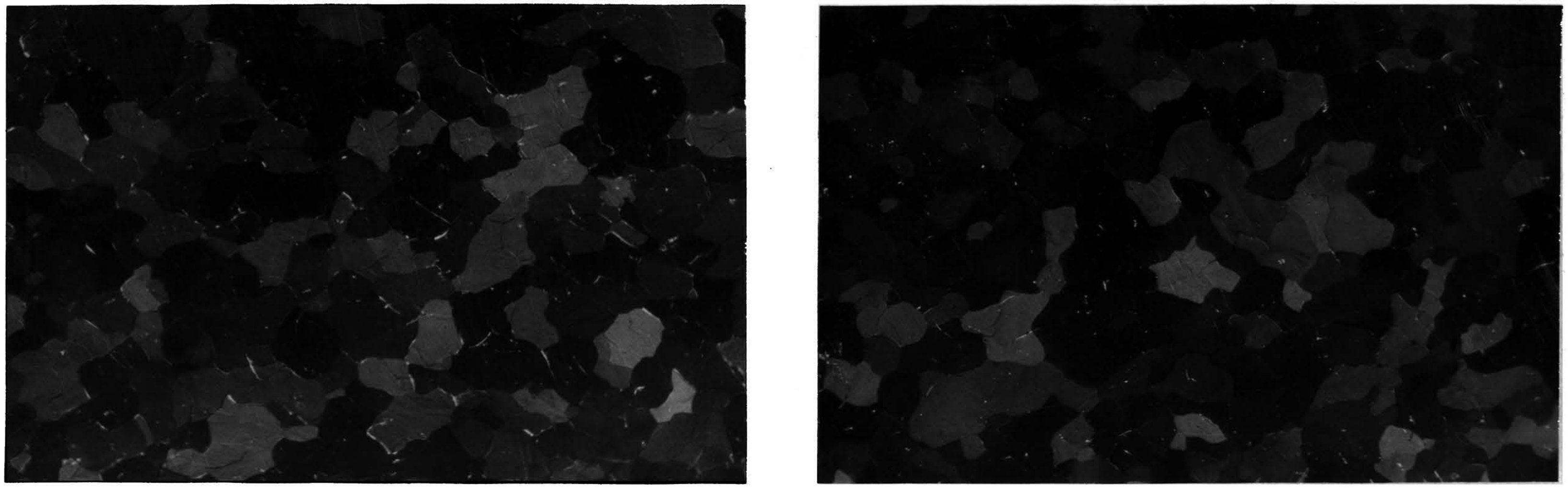
Photographs "b" and "d" show recrystallized grain boundaries to be etched. Etched remnants of the original cold worked structure are also present. Slight etching was noticed in all samples during heating and may have been caused by a faster vaporization rate at grain or twin boundaries. Surface tension effects may also have added to the etched appearance.

Several other differences in the completely recrystallized structures in Figure 19 should be mentioned. Photographs "b" was taken after the sample had cooled from 196°C to room temperature. Photograph "d" was taken at 225°C. The better contrast and brightness of photograph "b" results from photographing



a. Cold worked structure of 151°C sample.

c. Cold worked structure of 162°C sample.



b. Recrystallized structure of 151°C sample.

d. Recrystallized structure of 162°C sample.

Figure 19

Comparison of the cold worked and recrystallized structure for the 151°C and 162°C Zn-Mg-Al runs.

the sample at room temperature. Cooling the sample to room temperature has also made the etched grain boundaries more prominent. Photograph "d" shows numerous small white spots which represent intermetallic phases. Some spots are present at recrystallized grain boundaries, while other spots are arranged in a network bearing no relation to the recrystallized structure. The high temperature reached (225°C) has apparently caused the appearance of these spots.

Figure 20 is the Arrhenius plot to determine the activation energy, "E", for the recrystallization of the Zn-Mg-Al alloy, the slope of which is -5110. Calculation of "E" is shown below:

$$\text{Slope} = \frac{-E}{2.30R}$$

$$E = -(-5110)(2.30)(R)$$

$$E = 23 \text{ kcal}$$

In selecting the points through which to draw the straight line the 162°C run was not considered. This seems reasonable when considering the abnormal behavior of the 162°C recrystallization curve. In order for the 162°C points to fall on the straight line drawn, a higher recrystallization rate would have been necessary for the run. The same remarks made regarding the accuracy of the Arrhenius plot for pure zinc also apply to Figure 19.

Figure 21 is a sequence of photographs for the 162°C run. When comparing photograph "a" with photographs representing later stages of recrystallization, an increase in the number of white spots if found. This was also noted when observing samples of

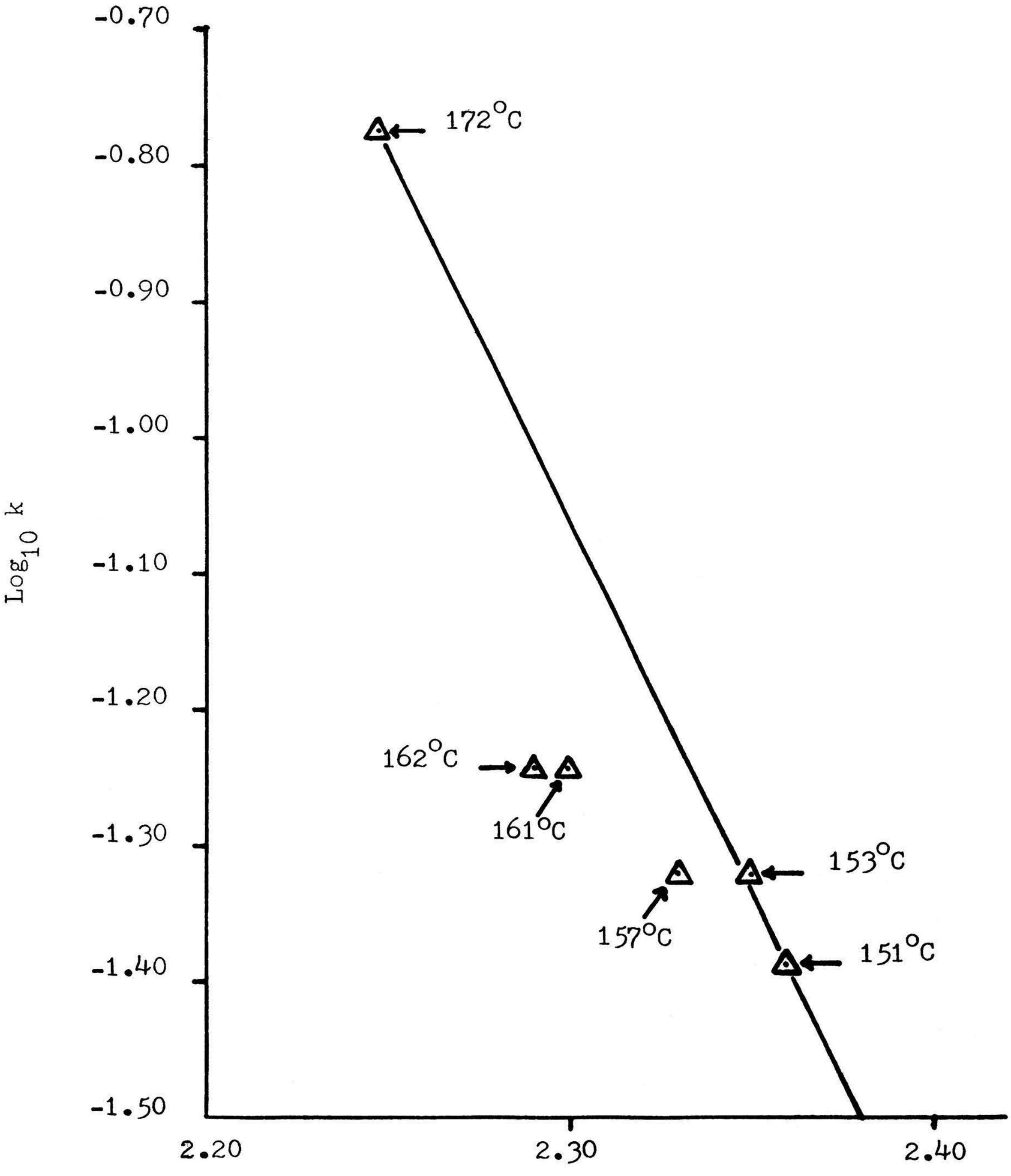


Figure 20
Variation of recrystallization rate of
Zn-Mg-Al alloy with temperature.

a. Prior to heating in hot stage.

c. 5.50 minutes

e. 24.27 minutes

b. 2.67 minutes

d. 11.42 minutes

f. 28.25 minutes

Figure 21
Sequence of selected photographs during the recrystallization of Zn-Mg-Al alloy at 162°C Time elapsed since the beginning of recrystallization shown for each photograph. Polarized light. 55.4x

pure zinc which had not been properly polished and were pitted. Apparently, very thin films can mask pits which are actually present beneath the film layer. During heating the film is destroyed and the pits open. The success encountered in polishing the Zn-Mg-Al alloy without pitting is probably due in part to the formation of thin films.

As shown by the isothermal recrystallization curves in Figure 18 (Page 62) recrystallization was not complete for the temperatures used. It was found that 195°C was necessary for complete recrystallization to occur.

VI. DISCUSSION AND CONCLUSIONS

The observations made by Brinson and Moore[9] and Brinson and Hargreaves[10] when using a hot stage to follow recrystallization in pure zinc were also noted in this investigation. They are as follows:

1. New grains form preferentially at grain boundaries and form to a lesser extent in twinned regions.
2. Twins have an unpredictable effect during recrystallization, sometimes restricting the growth of a newly formed grain and at other times having no observable effect on a growing grain.
3. Grain growth is irregular and not constant with time.

Additional observations were made during this investigation which were not apparent in the work of the above authors. The larger field of view used in this investigation probably enabled these observations to be made. Although new grains did form preferentially at grain boundaries, intersecting grain boundaries were the most probable sites for nucleation. Figures 17 (Page 60) and 21 (Page 67) show this tendency.

It was often noted that small, isolated grains which appeared to have an identical or similar orientation under polarized light would often grow and coalesce into one large grain. Whether or not any particular significance can be associated with this observation is not certain. A simple explanation, and no doubt a valid one in most cases, is that the irregular surface of a grain growing beneath the polished surface is first visible as small, isolated spots; however, some instances were found where the maximum distance between the isolated nuclei was greater than the diameter of any recrystallized grain on the polished surface; consequently, the recrystallized grain size would have to be larger beneath the polished surface in order for the small grains to represent portions of one larger grain.

The two white grains in the lower left portion of photograph "f" (Figure 17, Page 60) have formed by the merging of smaller isolated grains. Photograph "e" shows that the larger white grain has formed by the coalescence of three isolated grains. Photographs "c" and "d" show that the smaller and brighter white grain has formed by the coalescence of two isolated grains.

If the small isolated grains are not portions of one larger recrystallized grain, two possible conclusions would seem to be in order.

1. Recrystallized grains are not necessarily the result of the formation of one nucleus and the subsequent growth of this nucleus, but can represent a coalescence of several grains which have had the capacity to recrystallize with an identical orientation.
2. If the grains which coalesce to form one large recrystallized grain do not have the same orientation, the resulting recrystallized grain is not a single grain, but a "composite".

During very slow heating of pure zinc and Zn-Mg-Al samples in an attempt to determine the lowest temperature at which recrystallization occurred, it was noted that some twin bands would broaden slightly. This broadening occurred at temperatures considerably lower than the temperature of initial recrystallization. It seems probable that twin bands may undergo stabilizing structural changes before recrystallization begins. This would explain the resistance which twinned areas frequently showed toward recrystallization.

Brinson and Hargreaves[10] in directly observing recrystallization in slightly deformed polycrystalline zinc, found that indentation in the central portion of untwinned grains would form new grains, but that the grains had little capacity for growth. On the otherhand, grains formed by indentation at grain boundaries showed considerable growth. They concluded that deformation is inhomogeneous and that central portions of a grain are not deformed as much as portions adjacent to grain boundaries.

The above conclusion was supported in this investigation. It was frequently observed that a grain would completely recrystallize with the exception of a small portion in the interior of the grain. These remnants of unrecrystallized material appeared as "islands" and frequently required high temperatures to be reached before they would recrystallize.

Comparison between the 65°C isothermal recrystallization curve, nucleation curve, and grain growth curve for pure zinc (Figures 14, 15, and 16, respectively) shows clearly the maximum recrystallization rate is accompanied by maximum nucleation and grain growth rates. The grain growth curve is of particular interest as it reveals the manner in which growth rate changes with temperature. This curve disproves the early assumption in grain growth studies that the largest recrystallized grain present represented the first grain which had formed. This assumption was used to obtain the rate of grain growth by taking the slope of a grain diameter vs. recrystallization time plot.

The above method of determining the rate of grain growth would give a value too small as the early recrystallization times at which grain growth was slow would be included. Activation energies calculated by the use of such rates would be too high.

Activation energy values obtained for the pure zinc and the Zn-Mg-Al alloy, 29 kcal and 23 kcal, respectively, are in disagreement as the activation energy for the alloy should be higher. This discrepancy can be explained by the experimental difficulties mentioned in the experimental results. It should also be noted that the recrystallization which occurred prior to annealing the pure zinc in the hot stage would act to increase the activation energy obtained. The high recrystallization rate shown by the 76°C sample, which recrystallized very little prior to annealing in the hot stage, indicates that recrystallization during fabrication had caused a decrease in the recrystallization rate and hence an increase in activation energy.

The white spots associated with the recrystallized grain boundaries of the Zn-Mg-Al (Figure 19, photograph "e", Page 64) alloy are hard to explain as the opening of polishing pits during heating. Although the author has no knowledge of the heat treating characteristics of this alloy, it is probable that the high temperature reached (225°C) may have caused precipitation of intermetallic phases at the recrystallized grain boundaries.

All of the recrystallization data gathered in this investigation were obtained by observations on a free surface. No attempt will be made to theorize as to how recrystallization on a free surface would compare with recrystallization on an internal section of the sample, as no data was accumulated to make a comparison. Investigations by other researchers regarding this subject have been limited and contradictory.

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VITA

Roy Ashley Smith was born April 24, 1935 in Kankakee, Illinois. His secondary education was obtained at the Effingham High School, Effingham, Illinois. He received his college education at the University of Colorado, Boulder, Colorado; Southern Illinois University, Carbondale, Illinois; University of Missouri, Columbia, Missouri; and the University of Missouri School of Mines and Metallurgy. In August, 1958 he received a Bachelor of Arts Degree in Geology from the University of Missouri. A Bachelor of Science Degree in Metallurgical Engineering was granted to him by the Missouri School of Mines and Metallurgy in June, 1960.

After receiving his Bachelor of Science Degree he worked as a metallurgical engineer for Kaiser Aluminum and Chemical Corporation in Newark, Ohio. In September, 1961, he returned to the Missouri School of Mines and Metallurgy to begin work toward a Master of Science Degree in Metallurgical Engineering.

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