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HIGH TEMPERATURE ELECTRON MICROSCOPY

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HIGH TEMPERATURE ELECTRON MICROSCOPY

Gareth Thomas

April 1965

I. INTRODUCTION

Since the first high temperature stage for transmission electron microscopes was described in 1958⁽¹⁾ there have been only a few hot stage experiments reported.⁽²⁻⁶⁾ The first described the annealing out of dislocation loops by climb in aluminum⁽²⁾ and this technique was subsequently extended to studying the effects of magnesium additions on the climb rate.^(5,6) These kinetic measurements enable the self-diffusion activation energy to be determined and also the binding energy between vacancies and solutes to be estimated. Only two papers utilizing this technique appear to have been published on phase transformations, both of which were concerned with nucleation and growth processes in Al-Cu⁽³⁾ and Al-Ag.⁽⁴⁾ The rates of dissolution of precipitates were measured using movie techniques by which the activation energies for diffusion and the diffusion coefficients were estimated.

It is somewhat surprising that hot stage electron microscopy has not received wider attention. Experimentally, the technique is a little more difficult than normal microscopy and often necessitates at least two persons to carry out the observations, but this is not an overwhelming objection. The possibilities for hot stage work are enormous and it is very exciting to observe directly solid state phenomena such as dislocation climb, and phase transformations. The educational aspects are not to be neglected and it is a measure of the remarkable progress that has been made over the past eight years that now, in class, it is possible to show students dynamic phenomena taking place inside solids. Even heterogeneous precipitation at lattice defects has been recorded and many of the theoretical predictions concerning nucleation and growth have been

confirmed.

The electron microscope is unique in that it is the only technique which enables us to see inside solids and is thus preferred over thermionic emission or light microscopy which reveals only surfaces. Dynamical changes due to temperature which occur both at surfaces and inside the material can thus be observed directly. However, there are also possible objections. Since specimens have to be very thin (less than 1μ) to be electron transparent one is dealing with essentially a two-dimensional object so that surface diffusion becomes important. Thus, what one sees in such specimens may not be typical of bulk behavior. However, any single technique does not give the complete answer to a problem and has to be used in conjunction with others.

Although papers are available describing hot stages and some applications (refs. 1-9), a detailed analysis of procedures, contrast changes, etc., has not yet been set down in print. The invitation to prepare this paper has afforded me such an opportunity and it is hoped that, as a result, metallographers will be enticed to use the technique more often.

Some of the factors that need to be considered here include 1) temperature measurements, 2) coping with all the changes that occur on heating, such as contrast, specimen drift, beam drift, etc., and problems of interpretation, 3) contamination problems, and 4) recognizing possible surface effects and effects not representative of bulk behavior.

II. HIGH TEMPERATURE STAGES

Standard, nontilting, hot stages are available with most of the

modern electron microscopes and enable object temperatures of up to 1000°C to be attained. Little is known of the relative performances of each type of stage and most of the author's experience has been with an experimental stage^(1,3) and the standard stage for use with Siemens Elmiskop I microscopes.

All commercial hot stages are designed on the furnace principle and the specimen is not heated directly. It is very important that the design be such that rapid changes in temperature can be effected, because many dynamic processes occur so rapidly it may be impossible to carry out an experiment if the heating up or cooling down times are long, i.e., for furnaces that are thermally massive. There are thus advantages in experimental stages, such as that described by Whelan.⁽¹⁾ In this type of stage the specimen is mounted on a heating grid consisting of a 75 mesh screen of stainless steel which hangs freely in the cartridge. Thus, as soon as current passes through the grid the specimen heats up very rapidly and conversely when the current is switched off the specimen cools rapidly. With such a stage it was possible to solution heat treat foils of Al-Cu alloys in the microscope.⁽³⁾ Over the past few years we have used the standard manufacturer's stage in the Siemens Elmiskop I which has proved to be very satisfactory. The heating and cooling responses of this stage are described in section III.

Figure 1 is a cross section of the Siemens hot stage specimen cartridge showing the various features. The specimen is placed above the Pt cap and the arrangement inside the furnace is such that the object reaches the same temperature as the screw cap. The Pt-Ir furnace is insulated from the cartridge with a ceramic piece which is quite

delicate. It is very important to handle the stage with care at all times. The pressure spring 1 ensures that all the parts keep fitted together during expansion on heating. In order to avoid setting up interference fields which modify the field of the objective lens, the heating coil is bi-filar wound and is insulated with alumina. The heater leads are welded to two platinum contacts so that the heating probe which fits in place of the stereo drive on the front of the column (see Fig. 2) makes electrical contact to the heater when in the inserted position. Because of this feature the stage is not tiltable. The constant power to the furnace (0-12V, 1 amp. max.) is calibrated such that the input power can be used to measure the temperature. This is described in section III.

During heating of the specimen, because of thermal expansion, the object will be observed to move so that the operator must keep the specimen translation controls adjusted in order to observe continuously the same area. For the rotation-symmetrical construction of the cart-ridge, most of the movement takes place along the optic axis, i.e. the magnification increases. This amounts to about 5% at 1000°C so that focusing adjustments must also be made. If the furnace windings set up interference fields in the objective pole-piece, beam deflections may also occur. Thus, in practice the following microscope adjustments may have to be continuously made, in addition to maintaining the contrast constant (as will be described in section VII):

1. Position of specimen adjusted by translators
2. Focus of objective lens
3. Centering the beam with condenser translators

Consequently, it is very helpful to have two persons working together during hot stage experiments. The particular procedures for mounting specimens in the heater cartridge and for inserting and removing cartridges and heater probes on the microscope are described in detail in the manufacturer's instruction manuals. These should be followed carefully. Individually constructed stages will all be slightly different and have their own idiosyncrasies and the advice of the designers should be sought with regard to the most efficient way of using them. There have been many stages described in the literature, in particular, references (1, 7-9) should be consulted. Some of the later designs make provision for tilting and/or tilting-rotation of the specimen during heating.⁽⁸⁾ This is of great advantage for maintaining contrast as described in section VII. However, the use of gun tilting is often as effective as specimen tilting.

Hot stages must be designed so that no appreciable heat is lost and convected to the objective pole piece, otherwise, losses in magnetization and changes in focal length will occur. Also, the geometry of the field may be changed if the top of the pole piece is hotter than the bottom and this can lead to spherical aberration and decrease of resolution. In most cases a shorter heating cartridge than the normal specimen holder is employed to minimize heat losses to the pole piece. This results in operating at slightly larger focal lengths of objectives. With the Siemens hot stage the magnification is 85 to 90% of the normal value, hence, it is recommended that the magnification be recalibrated (in the usual way⁽⁹⁾).

III. TEMPERATURE CALIBRATION

One of the major disadvantages of the technique is the difficulty (in most cases, impossibility) of measuring the temperature directly of a particular specimen during an experiment. Due to space and design difficulties, thermocouples cannot usually be attached to the specimen when it is in the stage. It is essential, therefore, to precalibrate the heating stage prior to a set of experiments. Even when this is done the actual specimen temperature is still not known precisely. A number of calibration methods can be used, viz. 1) using a special specimen as a thermocouple, e.g. an evaporated bimetallic film (e.g. (Ag-Pd⁽¹⁰⁾) or Cu-constantan,⁽¹¹⁾ 2) materials of known melting or phase transformation points,⁽¹²⁾ or 3) by calibrating the power input to the furnace. The latter technique is used in our laboratory and will be briefly described here. First, however, it is necessary to consider beam heating.

Beam Heating

The specimen is heated during normal operation because of energy losses (mainly through inelastic collisions) occurring during electron transmission. All the factors leading to enhanced inelastic scattering, e.g. high atomic number, thick specimens, and low energies of the incident beam, will raise the specimen temperature. The temperature also depends on the volume irradiated, the size of the condenser apertures, and the current density of the beam. The equilibrium temperature then attained by a specimen depends on the fraction of electron energy converted into heat, and partly on the amount and efficiency of heat removal. The latter depends on the stage construction and materials used, as well as upon the thermal conductivity of the specimens. An increase in

conduction away of heat is achieved by mounting specimens between two copper grids. Thus, metallic foils remain at relatively low temperatures ($< 100^{\circ}\text{C}$) whereas ceramic specimens may heat up to several hundred degrees under the same operating conditions.

Stojanova and Belavtseva⁽¹⁰⁾ used a Cu-constantan specimen as thermocouple and investigated the temperature rise under various conditions. Their main conclusions were as follows:

a) Effect of Accelerating Voltage and Thickness

An increase in kV leads to a lower specimen temperature, but increasing the thickness of a specimen to the transparency limit markedly increases the temperature. These results are expected because the energy loss of electrons (i.e. the amount of inelastic scattering) is greater, the lower the voltages and the thicker the sample.

b) Area of Illumination

This is a very important factor. If the radius of the irradiated area of a conducting specimen is kept below about 15μ , the temperature rise does not exceed 10°C for normal current densities used in microscopy (up to 10 amp-cm^2).

Watanabe, et al.⁽¹⁰⁾ also confirmed the latter conclusion by using foils of Ag-Pd as thermocouple specimens.

Figure 3 is a plot of their results, showing the effect of irradiated area on temperature for foils of constant thickness, constant accelerating voltage and for a given condenser aperture (not stated in their paper), as a function of the current densities. It can be seen that for an illuminated

area of 5μ even at 10 amps-cm^2 the temperature is only $\sim 50^\circ\text{C}$. These results are in good agreement with theoretical calculations of the temperature rise.⁽¹³⁾

From a practical viewpoint, the availability of double condenser lenses is a boon for reducing the temperature rise of the specimen to a minimum. In the Siemens Elmiskop I, when condenser one lens is fully excited and condenser two is fully focussed, the beam diameter at the specimen has a minimum value of 2μ . In this case, for 100 kV operation with 600μ condenser aperture and using metallic foils of the usual thicknesses for transmission, the specimen temperature is less than 50°C . Gale and Hale⁽¹⁴⁾ have found with iron specimens that the maximum rise in temperature is 70°C in a Siemens Elmiskop I operated at 100 kV, $60\mu\text{A}$ using a 600μ condenser aperture and beam diameter of 2μ . Thus, it is essential to use double condensers to obtain the minimum beam diameter, so as to minimize heating.

However, a problem arises when using a fine focussed beam with hot stage operation, because the temperature of the irradiated area is usually greater than that of the foil as a whole. This can be checked by using alloys of known phase transition points. Set the stage temperature below the solvus point and find under what conditions the second phase dissolves. In this way the temperature effect due to beam heating can be corrected for in terms of aperture and beam sizes, current density, operating voltage, and specimen thickness. In other words sets of curves similar to those in Fig. 3 can be plotted, and the precalibration curves corrected (Fig. 4).

In order to minimize the complication due to beam heating the

following procedures are recommended. Either switch off the beam until ready to take an exposure (provided the foil does not drift too much on heating) or move the area of interest away from the beam until photography is needed. Beam heating thus leads to some uncertainty in the actual temperature of the area being photographed and is one of the main difficulties associated with obtaining reasonably accurate kinetic data for phase transformations and other dynamic events. However, if the above precautions are observed the temperature of the area being photographed can be estimated to within about 10° - 20° .

For following phase transformations without needing accurate kinetic data, pulsed beam heating is often of advantage. This method has been used for following the stages of ordering and precipitation of interstitials in bcc metals.^(15,16) Pulse heating is achieved either by increasing the beam current or by quickly removing and re-inserting the condenser aperture. Although little or no control of temperature is possible with this technique, various stages in transformations can be initiated, halted and then individually studied. In this way contrast and diffraction experiments can be done at each stage taking advantage of the normal goniometer specimen holder. In some cases, by using a hot stage the reactions proceed too quickly through the various stages to facilitate a complete interpretation.

Precalibrating Hot Stages

In our laboratory a constant voltage DC power supply (of the type normally used for electropolishing) is used for the temperature calibration of the hot stage specimen holder as a function of input voltage. Since the resistance of the heating element increases with temperature,

it was found that a constant voltage supply was better than a constant power supply because the desired temperatures could be attained faster this way, since the power input is initially larger as the resistance in the beginning is small. A voltmeter with the desired range of voltage scales may be connected in parallel to the output of the power supply, if the scales on the commonly used power supply are too small. Thus, the use of batteries and the inconvenience of charging, etc., can be eliminated.

The calibration is done in an evaporator under vacuum of the order of 10^{-5} mm or better to simulate conditions in the microscope. The results obtained depend on the position of the thermocouple in the specimen holder, but with a little care consistent temperature readings can be obtained. The thermocouple must be placed exactly at the specimen position.

The heating and cooling response of the Siemens hot stage is shown in Figs. 4a,b. In order to obtain a constant temperature, the foil must be heated for at least ten minutes. This gives rise to difficulties when rapid changes in structure occur over a short time. In this event the voltage is set to a higher value and then decreased to the desired temperature. The cooling rate with the Siemens stage is relatively slow over the low temperature range. As can be seen from Fig. 4a the cooling rate is most rapid over the first two minutes and falls very slowly below about 100°C . Thus, if martensitic transformations are to be observed one must work with alloys of $M_s > 100^{\circ}\text{C}$ and in which the critical cooling velocity is slower than about $200^{\circ}\text{C}/\text{min}$.

The calibration outside the microscope can be checked by running

the hot stage inside the microscope using specimens of known melting or phase transition temperatures. By this means it is found that pre-calibrations are accurate to about 20°C up to about 600°C, but the uncertainty increases above this value.

For quantitative work which depends critically on accurate temperature determinations, it is possible to age a foil outside the microscope and then examine the same area as a function of time. Special specimen holders are needed to avoid alloying or oxidation during aging since the foil should not be taken out of its holder once the experiment is started. One also has the advantage in these cases of using double tilt stages so that constancy of orientation and diffraction conditions can be maintained.

IV. EXPERIMENTAL ARRANGEMENT

Figure 2 is a photograph showing the set-up at the microscope for taking movies from images observed on the fluorescent screen. In some microscopes movie cameras are located below the screen as indicated in Fig. 5. In Fig. 2, the heater probe can be seen in the inserted position at the specimen chamber, and the former is connected to the pre-calibrated power supply. The movie camera is mounted on a tripod such that the axis of the camera is normal to the tilted fluorescent screen as shown in Fig. 5. In order to obtain maximum illumination a special Bell and Howell Angenieux f 0.95 lens, fully open, is used and the camera is placed as close as possible to the viewing window of the microscope. The lens carrying turret must be long enough to enable the camera to be focussed. We have found that with a Paillard-Bolex H1b camera a 5 mm spacer is needed for the arrangement shown in Fig. 5. The camera is

electrically driven through a variable speed motor (2-32 frames/sec) and is loaded with 16 mm movie film. Usually it is necessary to use Kodak Tri-X film, but with thin specimens of high contrast the slower speed, but finer grained Plus-X film can be used. For most experiments film speeds of 8-12 frames/sec are suitable.

In order to maintain adequate brightness, magnifications of up to 20,000X are recommended. When recording images from the fluorescent screen the highest intensities of the latter are needed. To calibrate the movie film a 1 cm mark can be made on the fluorescent screen. The total magnification can then be determined from the microscope magnification.

When viewing a developed film (e.g. for measuring changes in dimensions of a precipitate or dislocation loop) a movie projector of variable speed is required. Such a projector provided with a manual operator is very useful since one can then observe and make measurements on each frame one at a time. One way of measuring is to project the film, frame by frame, onto a white piece of paper and then draw in pencil each image of interest. The change in dimensions with time can then easily be obtained.

V. SPECIMEN CONTAMINATION

Adsorption

As all users of electron microscopes know, prolonged examination of the same area of a foil leads to general blackening and loss of resolution and contrast. This is due to contamination of the specimen from impurities in the vacuum, mostly arising from vapor, back-streaming from the diffusion pumps. Thus, in order to carry out different contrast experiments on the same area, it is essential to work as quickly

as possible. All the means which lead to reduced specimen contamination should be employed, and today many manufacturers provide decontamination devices and/or liquid nitrogen traps between the diffusion pumps and the microscope column. Vacuum grease on parts of the microscope should be avoided wherever possible.

The rate of contamination can be estimated from the Langmuir equation. The number of moles of a gas adsorbed on a solid surface per unit time and area is given by this equation:

$$Z = \frac{P}{\sqrt{2\pi M R T}}$$

and assumes that all gas molecules which strike the specimen surface are adsorbed and remain. In reality this will not be true, but the above expression does give the maximum possible rate. In the formula, M is the average molecular weight of the gaseous species, R the gas constant, T the absolute temperature and P the pressure of the gas. In the electron microscope, both surfaces of the specimen adsorb gas molecules, and assuming the average area of a specimen is one-third the area of its support grid then for a grid diameter of 0.23 cm, and assuming an average value of M to be 30 (carbon, hydrogen, oxygen, nitrogen, hydrocarbons, etc.), by appropriate substitutions the above equation reduces to

$$Z = \frac{31.8P}{\sqrt{T}}$$

Table I shows the results for a range of vacuum conditions and specimen temperatures. For a given vacuum, temperature has a small effect.

However, for the usual operating pressures (10^{-4} to 10^{-5} mm Hg) for all practical purposes during hot stage experiments, the contamination rate above 300°C is negligible and cannot be measured. At lower temperatures the rate can be estimated from the growth of the film deposited at the

TABLE I

Contamination Rate of a Specimen in the
Electron Microscope, Estimated From
the Langmuir Equation

Specimen Temp. °C	Operating Pressure (mm Hg)	Maximum Contamination Rate gm/cm ² /avg. foil/hr.
50°C	10 ⁻³	1.78 X 10 ⁻³
	10 ⁻⁴	1.78 X 10 ⁻⁴
	10 ⁻⁵	1.78 X 10 ⁻⁵
100°C	10 ⁻³	1.65 X 10 ⁻³
	10 ⁻⁴	1.65 X 10 ⁻⁴
	10 ⁻⁵	1.65 X 10 ⁻⁵
200°C	10 ⁻³	1.46 X 10 ⁻³
	10 ⁻⁴	1.46 X 10 ⁻⁴
	10 ⁻⁵	1.46 X 10 ⁻⁵

edges of the specimen.

The actual values obtained in Table I are probably not too meaningful because of the assumptions, but they do illustrate some important points and refer to maximum contamination rates under the conditions specified.

Some obvious conclusions can be reached from Table I.

1. The highest possible vacuum should be maintained during observations. Conversion to ultrahigh vacuum with vac. ion pumps may be desirable. Very fast pumping rates and the use of liquid nitrogen traps are recommended.
2. Large values of M decrease the contamination rate, thus silicone oils should be used in diffusion pumps. In our laboratory, Dow Corning 704 oil has been found to be very satisfactory and under normal operating conditions foils may be examined for 20 mins. or longer before contamination has any serious effect on resolution.
3. Contamination from water vapor present in freshly loaded plates can be avoided if the plates are always prepumped under high vacuum, before being charged to the microscope.
4. Although high temperature operation reduces the rate of contamination, the rate of diffusion of gaseous species into the specimen increases. Thus, due to the low activation energy for diffusion of interstitials in bcc metals ($\sim 20,000$ cal/mole for C in α iron), alloying during high temperature examination is possible.

It should also be mentioned that reactive metals may become contaminated with oxygen and/or hydrogen during thin foil preparation by

electropolishing or chemical polishing. In these cases and if the contamination rate in the microscope is high, ordering reactions or phase transformations due to interstitials may be observed during examination, e.g. O, N, C, H in Ta, Nb, V.⁽¹⁵⁻¹⁹⁾

Choice of Materials

Other sources of contamination include the materials used in the stage. Brass should be avoided because of the low boiling point of zinc at high vacuum. Figure 6 shows an effect when a brass specimen cap was used on the cartridge and heated to above $\sim 300^{\circ}\text{C}$. Zinc has evaporated and recondensed on the grid bars as whiskers. For similar reasons, magnesium and its alloys cannot be examined in the hot stage. The grids must also be carefully chosen to avoid alloying. Thus, the normal copper grids are unsuitable for supporting most foils if temperatures above about 200°C are to be employed. The difficulties due to these factors increase as the desired temperature increases. Platinum grids are recommended over stainless steel because of their better heat conduction. It is important therefore to thoroughly prepare for an experiment so as to avoid all possible sources of contamination. In certain cases, e.g. with the reactive metals, special thinning techniques may have to be used as described in the following.

Specimen Preparation⁽⁹⁾

It is beneficial to prepare uniformly thin flat foils for hot stage work. A micropolishing technique has been developed⁽²⁰⁾ whereby discs can be thinned down near the center. Such specimens have the advantage that they can be mounted in the cartridge without necessitating the use of support grids and thereby reducing possible contamination from

the grids and also providing good thermal contact in the holder (Fig. 1). An apparatus for this is shown in Fig. 7. The disc specimen, of diameter required for the specimen stage (3 mm for the Siemens), is stamped out from a sheet and mounted in a teflon holder such that the disc is concentric with the hole in the upper and lower halves and makes a liquid tight junction with both halves of the holder when the bolts are secured. A Pt contactor strip containing a hole of diameter greater than that of the disc makes contact with the disc and serves as the anode connection. The parts are assembled as shown in Fig. 7. A suitable electrolyte flows through a flexible tube from a reservoir placed about 18 in. above the holder. A pinch valve on the incoming electrolyte tube is adjusted so that the electrolyte flows and just wets the surface of the disc. As the specimen is electropolished a saucer-shaped depression is developed. The specimen is inverted and polishing is continued until, by observation with the binocular microscope (Fig. 7), a drop of liquid is first observed through the disc. Polishing is then immediately stopped before a visible hole appears otherwise large areas uniformly thin will be polished away and lost. The specimen is removed from the teflon holder, washed, and mounted in the cartridge using vacuum tweezers. By these means the foil does not have to be cut and is thus not mechanically deformed nor carelessly bent.

VI. CONTRAST

General Remarks

It seems unnecessary to go into details on contrast phenomena as these are now well discussed in the literature (see e.g. ref. 21 for review). Here some general conclusions are made regarding contrast and

how the latter may be modified by high temperature operation.

There are two important positions of the specimen as illustrated in Fig. 8. The first is for a tilted foil to achieve two beam conditions for contrast experiments and the second is for the reciprocal lattice plane exactly normal to the beam which is ideal for orientation determinations. In the latter case the centers of symmetry of spot and Kikuchi patterns coincide as shown in Fig. 9. In the former case, to avoid complications and to facilitate interpretation two beam situations must be employed, and the hkl Kikuchi must coincide with the hkl spot ($s = 0$) for dark field imaging.

At the exact Bragg condition the intensities of the transmitted and diffracted beams are complementary under non-absorbing situations. (22)
The dynamical intensities are then given by

$$|\psi|_T^2 = \cos^2 \pi \frac{t}{t_0} \quad \text{transmitted} \quad (1)$$

$$|\psi|_D^2 = \sin^2 \pi \frac{t}{t_0} \quad \text{diffracted} \quad (2)$$

where t_0 is the extinction distance for the operating reflection, (23)
and t is the foil thickness.

If the crystal is not at the exact Bragg condition, the reciprocal lattice point lies inside or outside the sphere. If the point lies inside the sphere, the deviation s in reciprocal space is taken as positive, and conversely s is negative when the point lies outside the sphere. These cases can be recognized in the diffraction pattern by the position of the Kikuchi line with respect to the spot. In the usual conventions, s negative means that the hkl Kikuchi line lies inside the hkl spot (as in Fig. 9) and vice versa for s positive (Fig. 16a).

At the exact Bragg case $s = 0$ and the Kikuchi line intersects the center of the diffraction spot (as in Figs. 15c,d). When s is not zero the diffracted intensity is modified to

$$|\psi|_D^2 = \left[\frac{\pi}{t_0} \right]^2 \frac{\sin^2 \pi t [s^2 + (1/t_0)^2]^{\frac{1}{2}}}{\pi^2 [s^2 + (1/t_0)^2]} \quad (3)$$

Thus, contrast from foils can be understood by considering the effects of structure on s , and t_0 and how the intensities are affected. Although a crystal may be set macroscopically at $s = 0$, lattice defects which distort lattice planes locally change the Bragg angle and the local value of s . If the displacement vector $\bar{R}$ of the defect is parallel to a reflecting plane $\bar{g} \cdot \bar{R} = 0$ and the defect is invisible. Most of the important effects concerning contrast from defects, including precipitates have been summarized recently. (21)

In thick specimens energy losses occur as a result of inelastic scattering so some of the electrons are absorbed and the intensities of the beams are reduced. In fairly perfect foils Kikuchi lines will be observed in the diffraction patterns (Fig. 9) and since these are essential in order to obtain foil orientations and crystallographic relationships accurately (see refs. 24,25), all microscopy should be done on relatively thick foils ($t >$ than about $3 t_0$) so as to obtain Kikuchi patterns.

Because of absorption the diffracted and transmitted beams are no longer complementary. The following effects (22) then occur

1. The bright field image is symmetrical (e.g. Figs. 10a, 16) with maximum intensity and contrast occurring for s slightly positive, e.g. Fig. 11 (i.e. the hkl Kikuchi lies just to the

outside of the hkl /spot).

2. The dark field image is asymmetrical (Fig. 10b); maximum contrast occurs at $s = 0$ (Fig. 11).

These results mean simply that the transmitted and diffracted waves are in phase at the top of the foil, but out of phase at the bottom. Hence, it is easy to determine which is the top or bottom surface.

It also follows from Fig. 11 that in bright field as soon as s becomes negative (one or other side of a half bend contour, whichever side is tilted to $<$ exact Bragg angle) there is a rapid loss of intensity and contrast. It is thus essential to work with relatively flat foils and to avoid bending specimens. Care should thus be exercised in foil preparation and handling.

Since the electrons are inelastically scattered at small angles they will be concentrated around the transmitted beam (the 000 spot in the diffraction pattern) and pass through the objective aperture. This adds to the background of the image and causes chromatic aberration. There is thus much benefit to be gained by using dark field microscopy with the gun tilted so that the diffracted beam passes down the optic axis. This avoids the spherical aberration and astigmatism that occur if the objective aperture is moved to obtain dark field images, e.g.

Fig. 10. The dark field image provides much useful information which might be missed in bright field, e.g. the detection of small precipitates,⁽²⁵⁾ and determination of the sign of the strain vector.^(26,27) Thus, one cannot urge too strongly that dark field imaging (by gun tilting) should be employed at all times. As shown in Figs. 10, 12, the operating reflection in dark field is the negative of that for bright field.⁽²⁷⁾ Thus, if $g = [200]$ is the bright field operator, tilt the gun so that the 000

spot moves in the $[200]$ direction until the $g = [\bar{2}00]$ beam is centered.

Effect of Temperature[†]

Sharp diffraction patterns occur from crystals because the atoms are arranged in regular positions so that coherent and in phase diffracted waves are produced. As the temperature is raised to the melting point, thermal vibrations cause the atoms to move from their regular positions so that successively scattered waves are no longer in phase. As a result there is a loss of diffracted intensity and the diffraction pattern becomes more and more diffuse until eventually, as in liquids or gases, very broad patterns are observed. There is also an increase in inelastic scattering and an added contribution to background intensity.

The intensity predicted by Eq. 3 is modified by the Debye-Waller factor, e^{-2M} , where M is related to the mean atomic displacement due to thermal vibrations. In effect the Debye factor is essentially a term that damps the lattice periodicity and decreases the atomic scattering. Upon heating there will be a loss in transmitted and diffracted intensities due to the Debye factor and an increase in thermal diffuse scattering which will add to the background. Thus, a foil will appear to gradually thicken as absorption is effectively increased, i.e. there will be a gradual loss of transmission as the temperature is raised. Thermal scattering is present even at 0°K due to zero point oscillations.

The "out of phaseness" of successively scattered waves due to thermal vibrations is equivalent to making s non-zero. Thus, from a contrast point of view, one can qualitatively take into account temperature effects by considering how s and t_0 are altered, and this leads to

[†]For a detailed discussion of theory see pp. 241-253 of ref. 23.

a good physical basis for understanding how to carry out hot stage experiments under controlled conditions.

1. Change in s on Heating

Under ideal conditions crystals may be set to a particular macroscopic value of s and the diffracted intensity is given by Eq. 3. As also pointed out by Howie and Valdré⁽²⁸⁾ thermal agitation will cause a spread in possible s values so s can be replaced by $s \pm (\overline{\Delta s})^2$ where $\overline{\Delta s}^2$ represents the mean square deviation from s because of thermal agitation.

The mean square vibration amplitudes for cubic crystals vary from about a factor of 2-4 from 0°K to 293°K. For example, the root-mean square vibration amplitude of silicon⁽²⁹⁾ changes from 0.075Å to 0.114Å which can have an appreciable effect on the value of s. Also, on heating the foil expands, so that Bragg's law is modified to:

$$2(d+\Delta d) \sin(\theta-\Delta\theta) = \lambda$$

the expansion Δd makes the Bragg angle smaller on heating so if the crystal is originally at $s = 0$, it becomes s positive on heating since the reciprocal lattice shrinks and the diffraction spot at P^* moves inwards to P_1^* , along the direction $O^* P^*$, as shown in Fig. 13b.

This effect is small, but measurable, particularly on Kikuchi patterns. With a crystal of $d = 2\text{Å}$ and assuming a coefficient of expansion of 10^{-5} , a change in temperature of from 20°C to 500°C increases d to about 2.005Å and decreases the Bragg angle by only 0.02° for $\lambda = 0.037\text{Å}$ (100 kV). For a Siemens Elmiskop I

operated at 100 kV using projector pole piece 3 this means a shift in the diffraction pattern relative to the 200 Kikuchi line of 0.2 mm (on the plate) since 1° tilt corresponds to about a 1 cm shift.⁽²⁴⁾ It is possible to compensate for this change in d and consequently s by changing the wavelength λ , i.e. the accelerating voltage. It would be useful to have microscopes with a continuously variable kV of ± 10 kV from 100 kV. However, this is not available now and is probably impractical.

The change in dimensions of a foil on heating are very small due to the small coefficients of expansion so that changes in t (Eq. 3) can be neglected.

A complication may arise with metal foils because they bend so easily. Unless a foil is perfectly flat the profiles will change on heating. Thus, a sharp saddle or valley may flatten out or vice-versa and then it will be impossible to keep the diffracting conditions constant throughout the experiment. Thus, one should not do hot stage experiments at or near sharp bend contours because these will move on heating. This results in loss of intensity and contrast particularly if s becomes negative (Fig. 11).

Some of the difficulties of working with severely buckled foils can be understood from Fig. 14 which shows a mound shaped buckle. θ represents the exact Bragg case, hence, by geometry it is easy to plot the s values across the bend. Such shaped crystals give rise to two bend contours corresponding to $+\bar{g}$ and $-\bar{g}$, outside of which are regions of good bright field image

contrast ($s > 0$). If on heating the foil the profile changes such as to increase the bend curvature, a serious loss of contrast will occur due to the large change in orientation. This might give a false impression of enhanced absorption. If the buckling is severe a three beam case (000, +g, -g) is obtained over the area imaged. Furthermore different contours and thus different $\bar{g}$ operators may cross the area of interest. Such changes are not of consequence when observing large precipitates, but in all cases where the image depends on diffraction contrast it is important to maintain the same diffracting conditions.

2. Change in Extinction Distance

The extinction distance t_0 is given by⁽²³⁾

$$t_0 = \frac{\lambda E}{Vg} = \frac{2\lambda E}{\Delta E_c}$$

where λ is the wavelength of incident electrons of energy E , Vg is the Fourier coefficient of the operating reflection $\bar{g}$ and ΔE_c is the energy gap at the Brillouin zone boundary corresponding to the same reflection (see Fig. 15). With increasing temperature, electrons are excited and may escape above their limiting energy level E_c^0 . The net effect is to make the Brillouin zone boundary "diffuse" and to lower the energy gap ΔE_c . Consequently, the extinction distance must increase on heating. This effect will also lower the diffracted intensity given by Eqs. 2 and 3.

Heidenreich⁽²³⁾ has also pointed out this fact and showed that with large atomic displacements the Fourier coefficients tend to vanish (i.e. the zone boundaries become very diffuse) leaving the diffuse component enhanced.

Since the intensity of diffuse scattering falls off with increasing angle, better images will be obtained by working in dark field of high order reflections, since the "signal to noise ratio" will be higher than for the transmitted beam. Figure 22 shows an example of a hot stage experiment done entirely in high resolution dark field (gun tilt).

Figure 16 shows the results of an experiment where the change in extinction distance was determined. Silicon was chosen because it does not bend and hence it is possible to maintain the same diffracting conditions throughout the hot stage work. Bright field imaging was employed because under these conditions the fringes are symmetrical.⁽³⁰⁾ In a non-tilting hot stage one has to choose an orientation close to $s = 0$, by viewing the sample. s can be made close to zero by tilting the gun (section VII). As shown by the diffraction patterns s was kept constant by adjusting the gun tilt observing the $0\bar{2}2$ spot and Kikuchi line in the diffraction pattern throughout the experiment. The calculated extinction distance for 220 in silicon is about $850\text{\AA}$. Figures 16a,b show the same stacking fault at room temperature and after 20 mins. at 430°C . There is one less black fringe resolved at the high temperature, and in this example there was about a 25% increase in extinction distance. This has been confirmed by subsequent experiments. This result cannot be explained by changes in s (by Δs). Such changes would effectively lower t_0 , hence the observed increase is a real effect of temperature on t_0 .

In the author's experience it has been noticed that for all

practical purposes there is no serious loss of intensity or resolution during heating experiments, provided the diffracting conditions are always kept the same. The procedures for doing this will be described in the following section.

VII. MAINTAINING CONSTANT ORIENTATIONS

As described earlier the most important effect as far as contrast is concerned is the change in s upon heating. Hence, it is essential to keep the orientation constant during an experiment. Figures 13a-d illustrate the main points to be brought out here. In (a) the two beam $s = 0$ situation is portrayed. After heating P^* moves to P_1^* , along $O^* P^*$ as shown in (b), hence, s becomes positive and the Kikuchi spacings decrease (compare Figs. 16a and b). s will continue to become more and more positive as the temperature is raised provided uniform thermal expansion and not buckling occurs. If the foil buckles such that it tilts clockwise the reciprocal lattice point rotates downwards about $O^* P^*$, along the arc $P_1^* R$ and could cause s to become zero again or even negative if appreciable tilting occurs.

In the absence of a tilting hot stage or of gun tilting facilities start the experiment for bright field work in orientations where s is negative and then during heating as s becomes more positive the contrast will improve.

If the stage is tiltable then as shown in Fig. 13c, tilting the foil restores the crystal to the desired s value (slightly positive for bright field, zero for dark field). If the foil cannot be tilted, the same result can be obtained by tilting the gun as shown in 13d.

Tilting the gun effectively translates the reciprocal lattice along a

desired zone and this is carried out by observing the diffraction pattern until the required s value is obtained. There are advantages to the latter method because the foil is unaltered and hence one does not lose the area during gun tilting. This is not usually true when tilting the foil. From a practical viewpoint it is almost essential to have more than one person involved in the experiment in order to accomplish everything that is required.

Constant diffracting conditions require frequent examination of the diffraction patterns. For specimen tilting stages tilt the foil until the Kikuchi lines sweep across the diffraction spot of interest. For gun tilting the Kikuchi line is relatively fixed and the spot pattern will sweep across the Kikuchi pattern. For all work where contrast needs to be maintained, work in two beam cases with s slightly positive (bright field, e.g. Fig. 16a), or $s = 0$ (dark field, e.g. Fig. 22). If orientation relationships are being determined, e.g. during phase transformations, exact foil orientations are required, i.e. symmetrical patterns such as shown in Fig. 9. In these cases constancy of orientation is achieved by keeping the centers of symmetry of Kikuchi and spot patterns coincident ($s < 0$) by tilting.

During heating experiments up to 700°C on flat foils, the maximum change in orientation is only $\sim 0.2^{\circ}$ which is quite small. However, 0.01° is sufficient to change the orientation enough to lose contrast. The translation of the gun shown in Fig. 13d does, of course, lead to non-axial illumination since the spot is moved a distance B off the optic axis. However, provided the angles are not great (less than about 0.5°), the increase in spherical aberration is negligible as can

be seen from Figs. 16a,b. However, it is very convenient to have a goniometer heating stage.

Finally, it is emphasized that for maximum benefit to be obtained from using the technique the researcher must be able to interpret the micrographs by proper correlation with diffraction patterns taken under controlled conditions as described above. The analyses for such interpretations are described in the literature (e.g. refs. 9, 21-27).

VIII. SUMMARY

In describing briefly some possible applications of high temperature microscopy in the following paragraphs all of the foregoing discussions must be borne in mind. In summary the procedures that are required are:

1. Special care must be taken to prepare flat specimens. In order to avoid stressing the foil, they should not be clamped between two grids.
2. Avoid contamination of the specimen by careful choice of materials and by high vacuum operation.
3. Calibrate the temperature as accurately as possible.
4. When doing an experiment
 - a) Maintain focus
 - b) Maintain centered illumination
 - c) Maintain specimen position
 - d) Maintain constant orientation by tilting specimen or gun; preferably work in dark field (gun tilted)
 - e) Switch off beam whenever possible

So far the areas where the technique has been profitably and quantitatively used, include investigations of diffusion controlled phenomena such as dislocation climb, ordering, and precipitation and dissolution. The field of shear transformations (martensites) seems to have been completely neglected. Spinodal transformations need also to be investigated. Studies of magnetic changes (observations of Bloch walls) with temperature are also possible. Recovery and recrystallization processes can also be followed, but the rates are slower in thin foils than in bulk specimens.

Apart from the difficulties of determining the true foil temperature, no serious problems from contamination are likely although it is emphasized that special care must be exercised when working with reactive metals (e.g. transition elements). Ultra high vacuum microscopes will reduce this problem to an absolute minimum. It is most convenient, to have a tilting hot stage although the gun tilt is often as effective for maintaining constancy of orientation. Finally, it should be emphasized that some observations on thin foils may not be representative of bulk behavior. Consequently, it is recommended as standard procedure that thin foil results should be compared to those from foils prepared from similarly treated bulk specimens (wherever possible). In certain cases, such as annealing out of loops, thin foils experiments have unique advantages.

The hot stage can be used to follow any or all phase transitions and could thus be applied to all the alloy systems. However, up to the present time only nucleation, growth and dissolution of phases in Al-Cu and Al-Ag alloys have been reported. In addition to phase transformations

dynamic processes such as dislocation climb can be followed which should provide further knowledge regarding creep and recovery.

Furthermore, the morphological, structural and crystallographic changes can be analyzed from micrographs and their selected area diffraction patterns. This is particularly useful for orientation determinations and even for structure analysis (e.g. during phase transformations),²⁵ The electron microscope is unique in providing this facility.

In view of the limited data available only a few applications are reviewed. These will be dealt with briefly in the following sections, and some further possibilities are mentioned. Due to space limitations readers should obtain more detailed information and discussion of the scientific implications of the examples used from the original papers.

IX. APPLICATIONS

Nucleation and Growth Phenomena

These transformations include all non-athermal (martensitic) reactions, e.g. spinodals, isothermal transformations, aging, etc. By means of hot stage techniques morphological and crystallographic relationships can be investigated. Competitive growth processes, where several phases are present can also be studied as well as determining whether reactions are allotropic or monotropic. Diffusivity measurements can also be made in localized regions.

1. Surface Effects

Two systems have been investigated in detail, Al-4% Cu by Thomas and Whelan⁽³⁾ and Al-20% Ag by Hren and Thomas.⁽⁴⁾ Whilst the aging processes in foils of Al-Ag were exactly the same as

those reported for bulk material by Nicholson and Nutting,⁽³¹⁾ aging of thin films of Al-Cu in the microscope was not representative of bulk material because in thin foils preferential surface nucleation of θ' was observed.⁽³⁾ Figure 17a-c is a sequence showing growth of θ' plates on the surfaces followed by precipitation inside the foil of θ with simultaneous dissolution of θ' , (competitive growth). Compare these to the structure of the aged bulk specimens shown in Fig. 17d.

It is important to know whether or not all the precipitates observed are on the surface. The following techniques enable this to be determined.

- a. Replicate the surface after aging and compare the replica with the structures from the foils.
- b. If precipitates extend right through the foil they should have some straight edges where the foil surfaces are intersected.
- c. In most cases the precipitates are associated with a well-defined habit plane so that trace analysis can be used. If precipitation is random all orientations should be present (e.g. θ' forms on {100}, compare Figs. 17a-c with 17d).
- d. If all precipitates are on the surface there should be no change in their density on changing the thickness of a foil (i.e. as the foil is traversed from the thin edges).

- e. Dark field images of strong matrix reflections will image black those areas occupied by precipitates if the latter run right through the foil (i.e. as if they were holes in the foil).

In the case of Al-Cu preferential surface precipitation is thought to be due to the transportation of copper atoms to the surface as a result of vacancy annealing of as-quenched foils.⁽³⁾ The problem is thus essentially one of nucleation so that the difficulties may be eradicated if specimens are pre-aged in bulk before thinning. Hot stage work can subsequently be carried out. In this way precipitates can be pre-nucleated so enabling growth processes to be followed which are representative of bulk annealing. Recent experiments on Al-4% Cu (Laird and Aaronson, private communication), have confirmed the latter prediction.

The selected area diffraction technique can be used to distinguish between different phases in the same area, e.g. θ' and θ were distinguished in the work on Al-4% Cu.⁽³⁾ The orientation relationships can also be found. The Kikuchi pattern must be used if accurate results are to be obtained.^(24,25) By observing paired Kikuchi lines in diffraction patterns of thick areas the axial ratios of non-cubic phases can be determined.⁽¹⁶⁾ Thus, recent work on the θ' phase in Al-Cu⁽²⁵⁾ using Kikuchi patterns has enabled c/a to be determined at 1.16 ± 0.02 which is smaller than the values reported by x-ray methods.

The work on Al-Ag⁽⁴⁾ showed that clusters of Ag atoms

were formed above the solvus temperature, and details of the growth mechanism of γ' plates were obtained.

2. Heterogeneous Precipitation

Direct observations have been made of heterogeneous precipitation on dislocations and stacking faults and confirm that nucleation rates are faster at dislocations than in the matrix.⁽⁴⁾ Figure 18 is a sequence from a movie film showing nucleation of γ' in Al-Ag at dislocations and subsequent growth by dislocations extending in the (111) planes. The velocity of the moving interfacial partial dislocation is determined by the diffusivity of silver. Conversely, on dissolution a precipitate finally leaves its dislocation behind after it has dissolved (see Fig. 19).

A new result was obtained on Al-Ag, viz. that intersecting precipitates could be stabilized up to 50° above the solvus temperature by forming low energy stair-rod dislocations. Dissolution occurs only when the stair-rod can be eliminated by nucleation of another partial dislocation. Figure 20 is a sequence showing such an event.

3. Estimation of Diffusivity from Precipitation Kinetics

Since the rates of nucleation and growth are generally quite low and would involve very long times at the microscope it is more convenient to study dissolution rates. The last stages in the lifetime of a precipitate is recorded on a movie film and subsequently the rate is measured from the film. If the process is diffusion limited the following

relation should hold

$$r^2 = -kDt \quad \text{or} \quad \frac{d(r^2)}{dt} = -kD \quad (5)$$

where r is particle radius, k is the rate constant and D the coefficient of diffusion of material from the precipitate.

Hence, the reverse of the growth case is assumed.⁽³⁾

The constant k depends on the shape of the precipitate.⁽³²⁾

If the shape does not change on dissolution, the spherical case is a good general approximation, whence^(3,4)

$$k = 2(c_s - c_e)/(c_c - c_s) \quad (6)$$

where c_c , c_s and c_e are the concentrations of diffusing material inside, at the surface, and at large distances from the particle. Frank⁽³²⁾ has given graphs from which k may be determined for spherical, cylindrical and plate shaped particles.

Combining the above equations, then

$$D = \frac{1}{2} \frac{(c_c - c_s)}{(c_s - c_e)} \frac{d(r^2)}{dt} \quad (7)$$

During the final stages of dissolution almost all the solute is in solution, hence c_e is about equal to the total atomic concentration of solute; c_s can be neglected in comparison with c_c . $(c_s - c_e)$ can be calculated from the slope of the phase boundary, i.e. it represents the supersaturation at a given temperature. For the dissolution case this represents the undersaturation so that the temperature above the solvus must be known in order to obtain the quantity $(c_s - c_e)$. In all cases surface effects are neglected.

In spite of the above approximations fairly good success in estimates of D were made on Al-Cu and excellent success was obtained for Al-Ag. Figure 21a shows the plots of x^2 versus time (where x is the length of a γ' plate) from which D was determined for Al-20% Ag and in Fig. 21b, D versus T^{-1} is a good straight line yielding an activation energy of $Q = 37.4$ (± 4 Kcal mole $^{-1}$) which is in very good agreement with other diffusivity data on Ag in Al.

Laird and Aaronson (private communication) have investigated the kinetics involved under competitive conditions, e.g. growth of θ at the expense of θ' and dissolution of θ' in Al-4% Cu. They used the simple form of the Zener-Hillert equation⁽³³⁾ to describe the lengthening on θ plates and shortening of θ' . For these cases the equations are similar, but not identical, to equation 7.

Their results showed that the calculated D values are about 1 to 1 1/2 orders of magnitude greater than those obtained by conventional diffusion techniques, i.e. that the growth rates are controlled by the interdiffusion of Cu and Al, but that the interdiffusion process is accelerated by some form of short circuit (which agrees with the results of Thomas and Whelan⁽³⁾). The short circuit path is undoubtedly along the surfaces of the foil. Observations on Al-Ag⁽⁴⁾ showed for growing or dissolving plates that the leading segments were always those at the surfaces, i.e. the ends of the plate develop a curvature towards the two surfaces

where the diffusion is most rapid. This will thus enhance the diffusivity compared to those precipitates growing or dissolving which are completely surrounded by the matrix.

Errors in the estimate of D arise from the following

- a. The approximations involved in the theory of diffusion used in the calculations.
- b. Difficulties of measuring precisely changes in precipitate dimensions
- c. Uncertainties in the temperature of the area being photographed.

It would be appropriate if the above techniques were tried on other systems to find out how far the steady state diffusion theory is applicable to dissolution processes.

The uncertainty in the data is mainly due to the difficulties of obtaining the temperature accurately. It is convenient to work with alloys where there is a large temperature interval between solvus and solidus so that D may be estimated over a wide temperature range, thus enabling a more accurate determination of the activation energy to be made.

4. Grain Boundaries

Another interesting area of research would be the investigation of morphology and kinetics of precipitation at grain boundaries, e.g. as a function of misorientation. Such experiments must be done in thick areas in order to obtain Kikuchi diffraction patterns from the grains involved so that the boundary angle can be calculated.

5. Changes of Coherency

Coherency strains from inclusions are visible in dark field images (two beam cases, $s = 0$) as black and white lobes of contrast divided by a line of no-contrast which is normal to the displacement vector.^(26,27) The sense of the strain field (i.e. vacancy or interstitial type) is determined from the direction of $\bar{g}$ with respect to the bright part of the image.⁽²⁶⁾ Figure 22 shows dark field examples from rods of phosphorus precipitates in P-doped epitaxially grown silicon. It can be seen that the rods show compressive strain fields. The possible loss of coherency on heating can be followed with hot stage experiments by noting changes in contrast maintaining constant orientation. Figures 22a-e show the decrease in volume fraction of the rods during heating; very few being left at 700°C. Although the density of particles decreases on heating there is no loss of coherency as the black-white image persists. Figure 22f shows that rods have re-precipitated after cooling down.

The nature of the interface between two phases and possible changes on heating can also be investigated. One way of doing this is to observe the Moiré image from overlapping crystals. Foil orientations must be chosen such that the habit plane of the precipitate is nearly parallel to the foil surface. Dark field techniques should again be employed to facilitate interpretation.

Structure and Orientation Changes

The diffraction pattern of the same area can be watched closely for detecting changes in structure on aging and to determine orientation relationships accurately by Kikuchi line analysis.⁽²⁵⁾ Useful Kikuchi patterns are only obtained from relatively thick and perfect foils.

Provided precautions are taken to obtain sharp diffraction patterns, the Kikuchi patterns, in principle, enable the coefficients of expansion, and any anisotropy of expansion in different directions, to be estimated. From Kikuchi patterns similar to those in Fig. 16, the measured changes in Kikuchi spacings using a densitometer are 1 - 1 1/2% over 400°C. The calculated change using the linear coefficient of expansion for silicon (7.63×10^{-6} at 20°C) is only about 0.33% which suggests that the measurements are not too meaningful. There are several difficulties, e.g. the foils are not free to expand uniformly in all directions because they are usually clamped at the edges in the specimen cartridge. Also, in order to avoid thermal stresses and buckling, foils should not be clamped between two grids. Thus, for such experiments, foils prepared by the technique described earlier (Fig. 7) should be used.

Transformations in Steels

There is nothing yet reported in the literature concerning direct observations of transformations in steels. There is no reason why such experiments cannot be done provided every care is taken to minimize contamination whilst the specimen is under observation. As shown by Table I if the vacuum is good ($< 10^{-4}$) and silicone oils are used in the pumps, no serious difficulties should be incurred for high temperature observations. Preliminary work by O. Johari has been carried out

in our laboratory on the tempering of martensite in Fe|30 Ni|0.3C. The results have shown that above 100°C the tempered product is always cementite. Aging in the microscope has been observed to produce more rapid growth of cementite compared to that observed after bulk tempering as was observed for Al alloys. It is probable that surface contamination and surface diffusion affect the reaction in the microscope. Figures 23, 24, 25 show a comparison of tempering done inside the microscope, thin foils aged outside the microscope and bulk tempered specimens. Figure 23d is an example when tempering has occurred due to beam heating caused by removal of the condenser aperture. Large cementite plates have formed in a matter of seconds.

The morphology and crystallographic relationships do not differ from specimens tempered inside or outside the microscope. Figure 24b shows a diffraction pattern of 24a from which the orientation relationship is

$$\begin{aligned} [211]_{\alpha} &|| [001]_c \\ [0\bar{1}1]_{\alpha} &|| [100]_c \\ [1\bar{1}\bar{1}]_{\alpha} &|| [010]_c \end{aligned} \quad \text{where } c \text{ represents cementite.}$$

Thus, the hot stage technique can be used to study morphological and crystallographic changes, but due to the probable higher rates of growth of Fe_3C in thin foils aged inside the microscope higher values for the diffusion coefficient of carbon are expected.

Some difficulties have been found with respect to outgassing of steel samples. In an attempt to transform an Fe|Ni|C martensite steel to austenite by heating to about 800°C a sample was observed to literally

"blow-up" during observation with the formation of blow holes and gas pockets. The trouble here is undoubtedly due to impurities in the material resulting from the manufacture of the alloy.

Ordering Transformations

It is now known that the interstitials C, N, O, H produce ordering in the refractory bcc metals. (15-19) A detailed investigation of Ta-C showed that the superlattice is tetragonal with $c/a = 1.128$ (determined from paired Kikuchi lines), of ideal composition $Ta_{64}C$. (16) The stages of ordering can be followed directly in the hot stage by aging quenched foils above about $500^{\circ}C$ or by pulsed beam heating. As yet, no kinetic data have been obtained, but the rate of growth of domain walls should correspond to the diffusivity of the interstitials.

The ordering in these systems is a transient stage in the transformation of $M_x I_y$ where M is the metal, I is the interstitial(s) and $M_x I_y$ refers to the next phase beyond the solid solubility limit. Van Torne and Thomas (15) transformed impure Nb to NbO via the ordering reaction and observed the transformation directly in the hot stage. Figure 26 shows examples of transformations in Nb-O and Ta-C alloys.

It is also possible to investigate directly substitutional ordering, but to the author's knowledge no papers describing dynamic observations are available as yet.

Self-Diffusion: Dislocation Climb

1. Perfect Loops

Sildox and Whelan (2) were the first to demonstrate directly the process of climb by annealing out perfect dislocation loops ($\bar{b} = \frac{1}{2} \langle 110 \rangle$) formed by quenching aluminum rapidly from near the

melting point. From data on the rates of shrinkage of loops the activation energy for self-diffusion was determined to be in the range of 1.2 to 1.3 eV.

Subsequently, Eikum and Thomas^(5,6) extended the work on Al to alloys of Al-Mg. One of the interesting features of these experiments was that in alloys supersaturated with Mg, vacancies could also be held in supersaturation since loops were observed to grow on annealing thin foils. In pure Al and unsaturated Al-Mg alloys loops always shrink indicating no supersaturation exists in the foil. The free surfaces act as infinite sinks so the loops are destroyed by boiling off vacancies to the surfaces. Figures 27 and 28 show examples of climb of dislocation loops.

The phenomenon is interpreted in terms of the climb theory due to Friedel.⁽³⁴⁾ If the loop does not contain a stacking fault the rate of climb is given by⁽²⁾

$$\frac{dr}{dt} = -\frac{1}{2} z \nu b \exp\left[\frac{-E}{kT}\right] \left\{ \exp\left[\frac{F_c b^2}{kT}\right] - \exp\left[\frac{F_s b^2}{kT}\right] \right\} \quad (8)$$

z is the coordination number (~ 11), ν the atomic frequency ($\sim 10^{13}$), $b = 2.86$ for Al and T the absolute temperature. $F_s = \frac{kT}{b^2} \log \frac{c}{c_0}$ is the chemical force due to vacancy supersaturation ($c - c_0$) which is zero during shrinkage, i.e. no supersaturation can exist if all vacancies go to the surfaces. E is the self-diffusion energy (the sum of formation and migration energies, E_f , E_m , respectively). If solute atoms are present which are bound to vacancies E will be reduced by the binding energy E_b .

If the rate of change of loop size is measured as a function of temperature, the activation energy is given directly by an Arrhenius plot of rate vs $(T^{\circ}\text{K})^{-1}$. An example for Al-5% Mg is shown in Fig. 29. Figure 30 shows the measured activation energies as a function of Mg content. It is expected that a sharp drop in activation energy will occur at the solubility limit ($\sim 2\%$ Mg at room temp.), because in supersaturated alloys the total vacancy concentration is much greater than in unsaturated alloys. (5,6,35) The results can be understood on the basis of vacancy trapping by magnesium atoms, and the binding energy is estimated to be ~ 0.2 eV at 5% Mg. (5)

The activation energy can also be determined from a single shrinkage sequence. The time t for a loop to shrink to $r = 0$ is related to the activation energy E by

$$t = t_0 \exp (E/kT) \quad (9)$$

where

$$t = r_0^2 (z v b^2 \alpha)^{-1} \quad (10)$$

α is $\sim \frac{F_c b^2}{kT} \cdot \frac{r}{b}$ (see eq. 8). For Al, Silcox and Whelan estimated $\alpha \sim 72$ at 161°C and ~ 64 at 200°C . A plot of r vs t will be parabolic, (see Fig. 31) and substitution of values in eq. 9 enables E to be determined. However, the accuracy of this method depends sensitively on the temperature; a 10°C error gives an error in E of 2%. Due to the difficulties of its measurement, rates at different temperatures should be used to determine E . Otherwise, aging should be done outside the microscope so that T can be measured to within 0.1° .

An important point with regard to measuring loops is that the diffracting conditions must be maintained constant because the size of the image depends on the sign of the quantity $(\bar{g} \cdot \bar{b})_s$.⁽²²⁾ The image of a loop is smaller than the actual loop for $(\bar{g} \cdot \bar{b})_s < 0$ and larger for $(\bar{g} \cdot \bar{b})_s > 0$.^(21,22,36) Thus, if half a bend contour crosses a loop during observation (see Fig. 14), s may change sign and the apparent size of the loop will change. If appreciable buckling occurs a different contour may cross the loop and then $\bar{g}$ changes. These problems can be avoided by carrying out the observations in the dark field image of constant $\bar{g}$ and at $s = 0$. However, experimentally this method is difficult unless at least two people work together.

Another technique which is useful when non-tilting stages are used is the following. In Al no climb is detected below about 150°C (this depends on impurity content) so if the foil is first heated, to say 120°C, most of the specimen drift and bending will have already taken place. A suitable area can then be selected for obtaining kinetic data.

2. Faulted Loops: Estimation of Stacking Fault Energy

In the case of a faulted loop* ($\bar{b} = \frac{1}{3} \langle 111 \rangle$) the stacking fault will assist the line tension in reducing the loop size by climb. The rate of shrinkage of a faulted loop is then given by substitution in eq. 8

$$\frac{dr}{dt} = -\frac{1}{2} z \nu b \exp\left(\frac{-E}{kT}\right) \left\{ \exp\left[\frac{(\gamma + f_c) b^2}{kT}\right] - 1 \right\} \quad (11)$$

* See ref. 37 for a review of loops in quenched metals.

where $F_c = f_c + \gamma$ and $f_c = \frac{Gb}{4\pi(1-\rho)} \frac{\ln r/b}{r/b}$ and γ is the stacking fault energy. This case differs from the case of an unfaulted loop (eq. 8) only by the term in the square brackets. Thus, it is possible to estimate γ by comparing the rates of shrinkage of perfect and imperfect loops of comparable size in the same area of a foil in the hot stage.⁽³⁵⁾ Since $\gamma \gg f_c$ in the exponential of (eq. 11) f_c can be neglected, particularly for large loops. Then by dividing (eqs. 8 and 11)

$$\frac{(dr/dt)_F}{(dr/dt)_P} = \frac{\exp(\gamma b^2/kT)_F^{-1}}{\exp(F_c b^2/kT)_P^{-1}} \quad (12)$$

where F and P refer to Frank and perfect loops. Figure 28 is an example of a comparative climb sequence in Al-1% Mg and Figure 31 is a plot of the respective rates. From such data γ for this alloy was found⁽³⁵⁾ to be ~ 200 ergs/cm². Edington and Smallman (private communication) reported a value for $\gamma \sim 280$ ergs/cm² in pure Al obtained from data on shrinking faulted loops (from eq. 11) and these results indicate that Mg has a substantial effect on lowering the stacking fault energy of aluminum.

Such climb experiments are useful for obtaining information on the stacking fault energies of metals which cannot be determined by the node method (i.e. for metals where $\gamma > 25$ ergs/cm²).

The comparative method (eq. 12) has the advantage of not depending sensitively on the value of E or T. γ can also be estimated from eq. 11 by measuring dr/dt at two different tempera-

tures. However, in this case an accurate knowledge of both E and T is required. For this reason, the latter method is not recommended unless foils are aged outside the microscope under accurately controlled conditions.

Recovery and Recrystallization

With the hot stage it is possible to observe directly climb, polygonization and recrystallization in cold worked metals. However, the annealing behavior of thin foils observed by hot stage techniques is often markedly different from that of bulk specimens. It is generally observed that polygonization and recrystallization occur at slower rates in thin foils (see e.g. refs. 38, 39). It is possible that some of the long range stress fields may be reduced in thin foils so that the driving force for recrystallization is lowered. Some care must be exercised, therefore, in proposing mechanisms of recovery and recrystallization based solely on thin foil observations.

Martensitic Transformations

Since most martensitic reactions in steel occur athermally and at high speeds these transformations can only be studied if the hot stage can be rapidly cooled when the power is turned off. As shown in Fig. 4a the cooling rate for the Siemens hot stage is several hundred degrees/min down to $\sim 100^{\circ}\text{C}$. Hence, steels must be chosen with $M_s > 100^{\circ}\text{C}$ and for which the critical cooling velocity is less than about $200^{\circ}\text{C}/\text{min}$.

If the foil is heated to the austenitic region care must be exercised to avoid contamination during the thermal cycle, otherwise, the concentration of interstitials will undoubtedly increase due to

their rapid diffusion into the foil at high temperatures. For experiments on martensite it may be necessary to use an experimental stage such as that described by Whelan⁽¹⁾ in order to obtain rapid cooling.

The crystallography of the shear transformation may be different in foils than in bulk material since in the latter case true three dimensional constraints impose boundary conditions.⁽⁴⁰⁾ Thus, in Nb-NbO the habit plane was found to be {110} in thin foils, but {201} in bulk.⁽¹⁵⁾ Also, Pitsch⁽⁴¹⁾ found in Fe-C and Fe-N alloys that the orientation relationships were different from those observed for transformations in bulk specimens.

Another factor is that the M_s temperature seems to be effectively raised by thinning down (similar to the grain size effect). Observations on steels show that the thinnest edges of foils may be martensitic, whereas the thicker areas are still austenitic. This effect can also be understood on the basis of the relaxation of the boundary conditions in thin regions.

Stacking Fault Energy from Node Measurements

So far the only pure metal which has been observed to have a low enough stacking fault energy to be measured using the node method (see e.g. ref. 42) is silver. Gallagher⁽⁴³⁾ and Loretto et al.⁽⁴⁴⁾ estimated the stacking fault energy from the formula⁽⁴⁵⁾

$$\gamma = \frac{n G b^2}{W} \quad (n = 0.25 \pm 0.03 \text{ for screws})^{(46)}$$

(where W is the inside radius of the node) and obtained average values at room temperature of $20 (\pm 6)$ ergs/cm² and $21 (\pm 7)$ ergs/cm², respectively. Gallagher further measured the variation of γ with temperature and found, as expected, that the stacking fault energy

varies with temperature only as the shear modulus and $|\bar{b}|$, since W did not change.

Although larger nodes are observed in alloys, due to their lower stacking fault energy, and it is easier to carry out hot stage work in such cases, difficulties in interpretation arise because of possible atomic rearrangements at the node during heating, e.g. de-segregation or order-disorder. Swann⁽⁴²⁾ observed that nodes collapsed in copper alloys on heating, but the causes for this phenomenon are incompletely understood at this time.

X. CONCLUSIONS

High temperature electron microscopy provides quantitative, new research and educational information and it is hoped that wider use will be made of the technique. Although only a few metallurgical applications have been discussed here there is no reason why attempts should not be made to investigate ceramic systems. Because of the present difficulties of accurately measuring the temperature of foils and because dynamic events occurring in thin foils may not represent the behavior of bulk materials, it is essential to compare hot stage results with those obtained from similarly treated bulk samples.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the assistance of my graduate students during the preparation of this paper. Thanks are also due to Mr. Larry Ernst for preparing some of the foils and for his attention to the microscopes and to Mr. John Blunden and the Technical Photography and Graphic Arts Division of Lawrence Radiation Laboratory. This work was done under the auspices of the U. S. Atomic Energy Commission through the Inorganic Materials Research Division of the Lawrence Radiation Laboratory. The award of a Miller Research Professorship is gratefully acknowledged.

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Figure Captions

- Figure 1 Cross section of the hot stage cartridge for use in Siemens Elmiskop I microscopes. (1) pressure spring, (2) contact yoke, (3) heating element, (4) furnace, (5) cap. Courtesy Siemens and Halske Ltd.
- Figure 2 Photograph of microscope arranged for hot stage work and ciné recording of the image observed on the fluorescent screen.
- Figure 3 Temperature rise of specimen due to heating (ref. 10).
- Figure 4 (a,b) Temperature precalibration curves for the Siemens hot stage (a) showing heating and cooling response, (b) steady stage temperature vs. voltage.
- Figure 5 Sketch showing arrangement for movie recording of dynamic events.
- Figure 6 (a,b) Bright and dark field images showing formation of zinc whiskers on grids due to volatilization of zinc from a brass cap after heating at about 400°C.
- Figure 7 Sketch showing arrangement for micro-electropolishing.
- Figure 8 Sketch showing orientation of specimen and diffraction patterns for (a) contrast work in two beam cases and (b) exact orientations. Notice s is < 0 in (b).
- Figure 9 Exact [111] orientation from a silicon crystal. Notice centers of symmetry of Kikuchi pattern and spot pattern coincide (compare to Fig. 8b).
- Figure 10 (a) Bright field image of stacking faults in cobalt; s slightly positive.

(b) Same area in dark field (gun tilt), $s = 0$. The bright field image is symmetric whilst the dark field image is asymmetric. Notice the greater resolution of the dark field image, and that $\bar{g}$ for dark field is the negative of g for bright field (see Fig. 12).

Figure 11 Rocking curves for transmitted beam (bright field) and diffracted beam (dark field) computed from the two beam dynamical theory with absorption (Howie and Whelan, ref. 22) Courtesy Royal Society.

Figure 12 Showing that the operating reflection for dark field (tilted gun technique) is the negative of that for bright field.

Figure 13 Sketches illustrating changes in contrast on heating.

- (a) original, foil at $s = 0$.
- (b) on heating foil expands, s becomes > 0 .
- (c) correction of (b) by tilting foil (to $s = 0$).
- (d) correction of (b) by tilting gun (to $s = 0$).

Figure 14 Diffraction from a slightly buckled foil. The lower part shows the two half contours which will be observed in the image.

Figure 15 One dimensional section through k space showing the energy of a crystal as a function of the component k_x . The energy gap ΔE_c gives rise to extinction due to interaction of electron waves of energies E_c^0 and E_c' (after Heidenreich⁽²³⁾).

Figure 16 Showing increase in extinction distance due to heating, silicon foil 202 reflection.

- (a) initial state s close to zero (see diffraction pattern).

(b) after 20 mins. at about 420°C.

Notice the number of fringes reduces by one at the high temperature. The diffraction patterns show that the same orientation has been maintained. Some spherical aberration is evident due to gun tilting (see Fig. 13d).

Figure 17 (a-c). Showing growth of θ' phase on foil surfaces during aging in the microscope at about 250°C. In (c) the temperature was raised whence θ nucleated and θ' dissolved. In (d) the structure of an aged bulk specimen is shown for comparison (aged 10 mins. 270°C).

Figure 18 Sequence from movie film showing heterogeneous nucleation of γ' in Al-20% Ag. (a) foil at 500°C, (b) after quenching, nucleation occurs on dislocations C, D, (c) growth of γ' plates. Two orientations have developed at D. The thickness increases by nucleation of partial dislocations - notice ledge at L in (c). Courtesy Trans. AIME (ref. 4).

Figure 19 Illustrating the reverse process shown in Fig. 18. Temperature ~ 500°C time sequence ~ 0.2 secs. Notice emission of dislocation upon complete dissolution (c,d). Courtesy Trans. AIME (ref. 4).

Figure 20 Showing interconnected γ' plates in Al-20% Ag. Temp. ~ 475°C. The configuration unwinds after a partial dislocation E has been nucleated near the stair-rod at A. Time sequence 0.1 sec. Courtesy Trans. AIME (ref. 4).

Figure 21 (a) Rate of dissolution of γ' plates in Al-20% Ag, from which the diffusion coefficient D is calculated.

- (b) Activation energy for dissolution of γ' plates, data obtained from Fig. 21a. Courtesy Trans. AIME (ref. 4).

Figure 22 Sequence of heating P-doped [111] silicon foil. The patches are due to oxide films.

- (a) before heating, notice strain contrast from rods lying along $\langle 110 \rangle$.
(b) $T \sim 350^\circ\text{C}$.
(c) $T \sim 450^\circ\text{C}$; some dissolution has occurred, but strain images are retained.
(d) dark field diffraction pattern showing $g = 220$, $s = 0$ is maintained; g is to the same side as the white parts of strain contrast images, hence the strain field is vacancy type.
(e) $T \sim 700^\circ\text{C}$: most of the rods have dissolved.
(f) after cooling down; notice re-precipitation of rods.

Figure 23 Examples of tempering thin foils of Fe|30 Ni|0.3 martensitic steel inside the microscope

- (a) 2 mins. at $\sim 200^\circ\text{C}$.
(b) same area, temperature raised to $\sim 280^\circ\text{C}$.
(c) 15 min. at $\sim 100^\circ\text{C}$; dark field showing twins with Fe_3C (white) on the twin planes.
(d) growth of Fe_3C due to beam heating.

Figure 24 Thin foil Fe|30 Ni|0.3C tempered in vacuum outside microscope.

- (a) 2 mins. at 200°C . (compare to Fig. 23a).
(b) inset shows diffraction pattern of (a). Notice oriented Fe_3C spots.

Figure 25 Foils of same alloy prepared from bulk specimen tempered in vacuum outside microscope.

- (a) tempered 2 min. 200°C. (compare to Figs. 23a, 24a).
- (b) dark field image of a cementite reflection shown in c.
- (c) diffraction pattern of (a) showing extra spots due to Fe_3C .

Figure 26 Ordering reactions due to interstitials in the bcc metals.

- (a) domains on {110} in Nb-O observed during beam pulsed heating experiments (ref. 15).
- (b) final stages of ordering showing domains in Ta-1.8 at.%C observed during beam pulsed heating experiments (ref. 16).

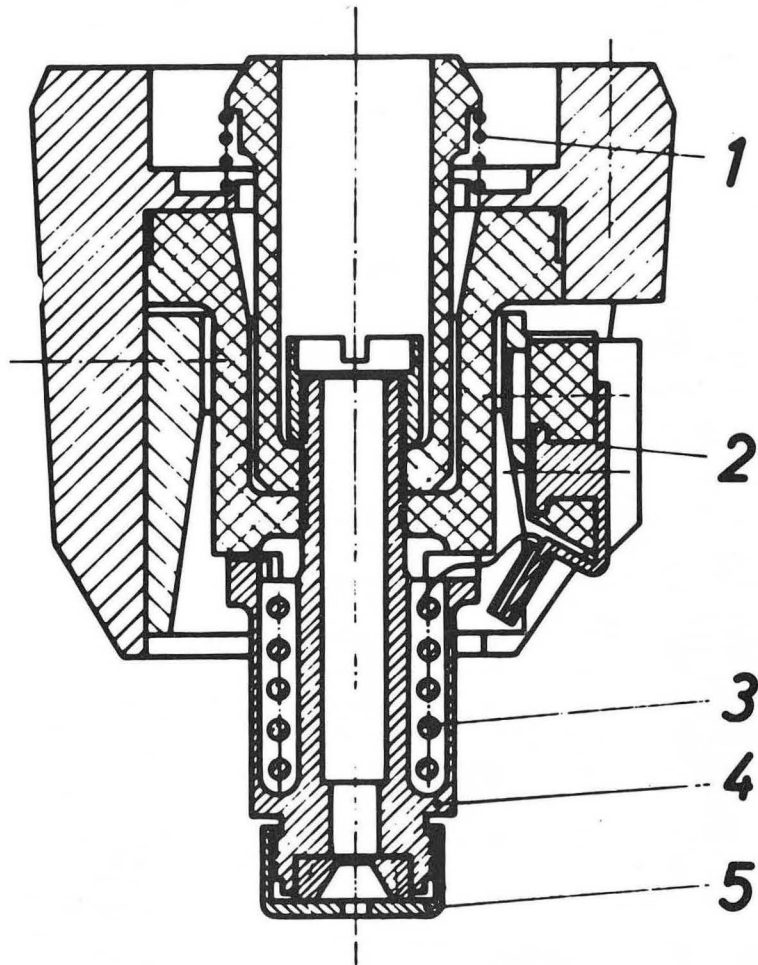
Figure 27 Sequence from movie film showing growth of loops by climb in Al-5% Mg (ref. 5).

Figure 28 Sequence from movie film showing shrinking Frank and perfect loops in Al-1% Mg. Time sequence is indicated (ref. 35).

Figure 29 Plot of growth rate of loops vs. $[T^\circ\text{K}]^{-1}$ in Al-5% Mg alloy (ref. 5).

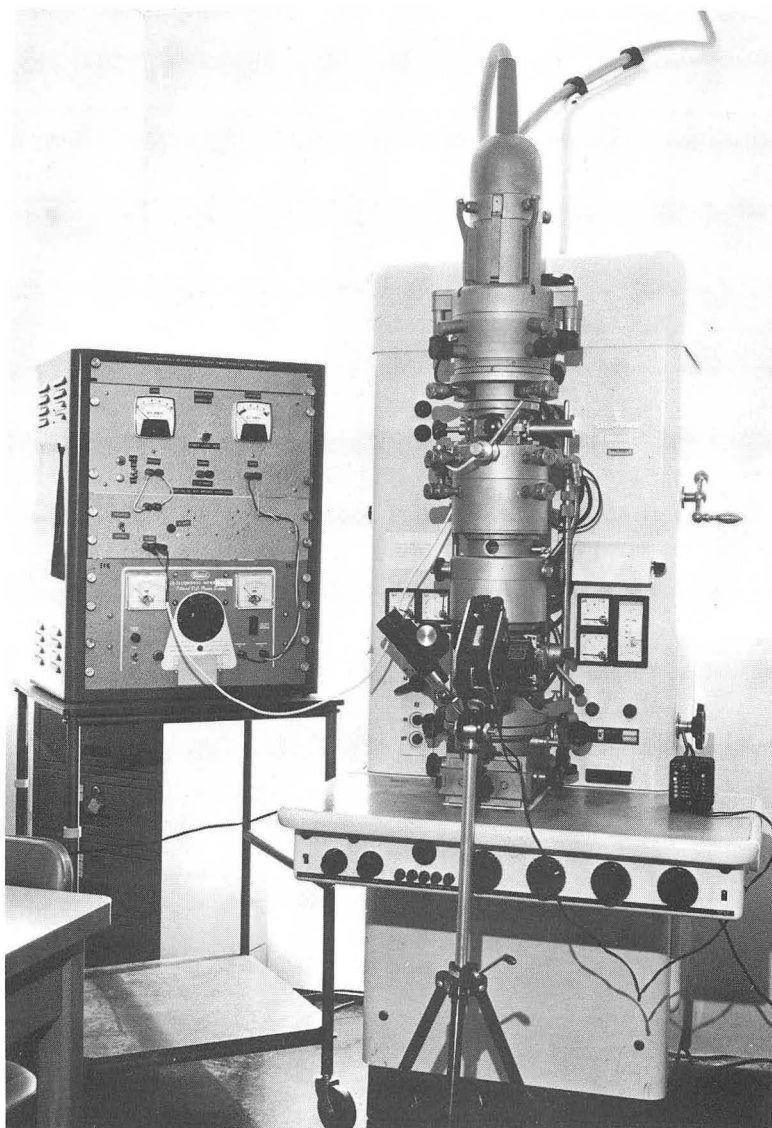
Figure 30 Values for the activation energies for climb in Al and Al-Mg alloys. The dotted line is a suggested variation of the activation energies vs % Mg. The value for pure Al is from ref. 2.

Figure 31 Plot of rate of shrinkage of Frank and perfect loops in Al-1% Mg. Such plots enable the activation energy for climb and the stacking fault energy to be determined (ref. 35).



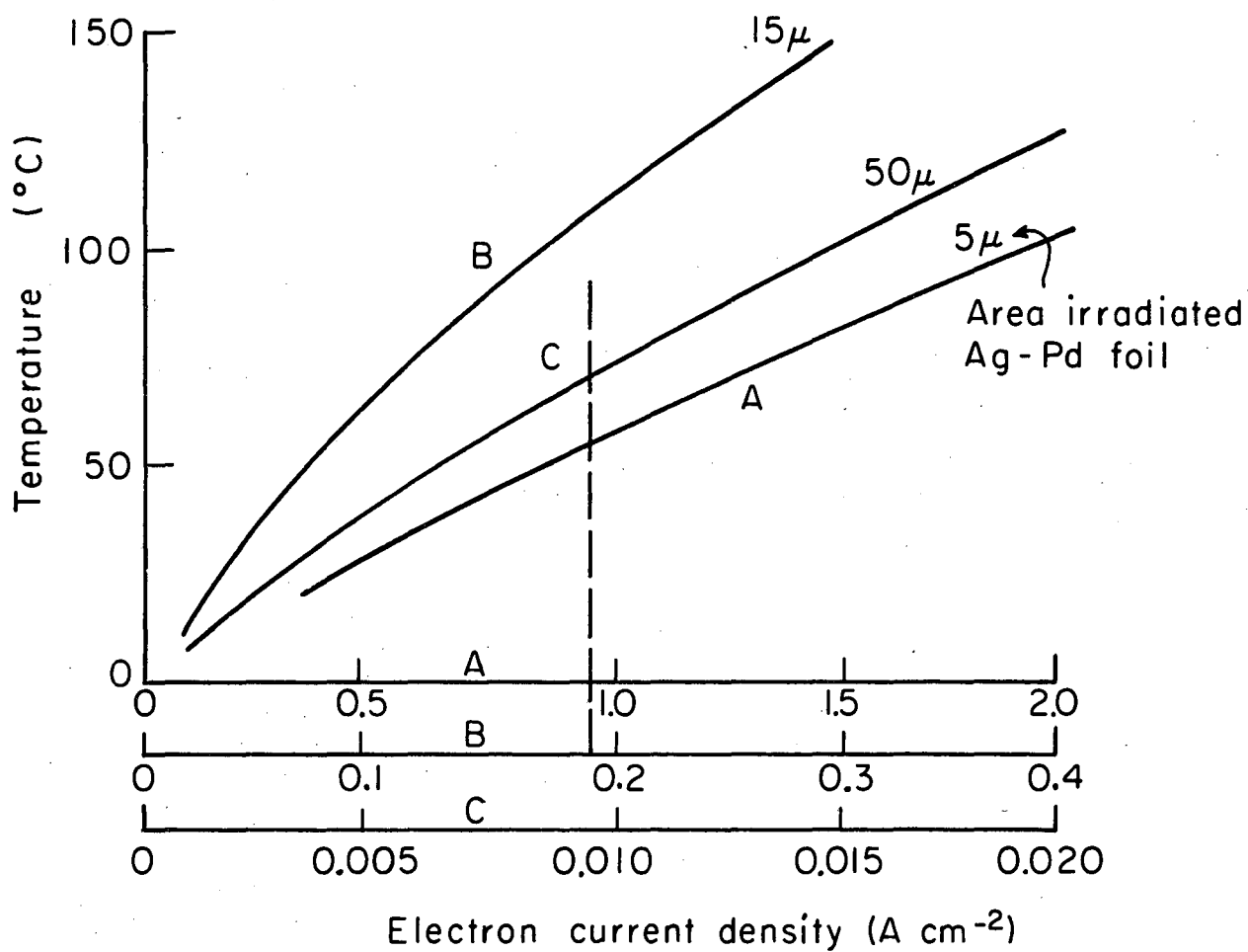
MUB-6075

Fig. 1



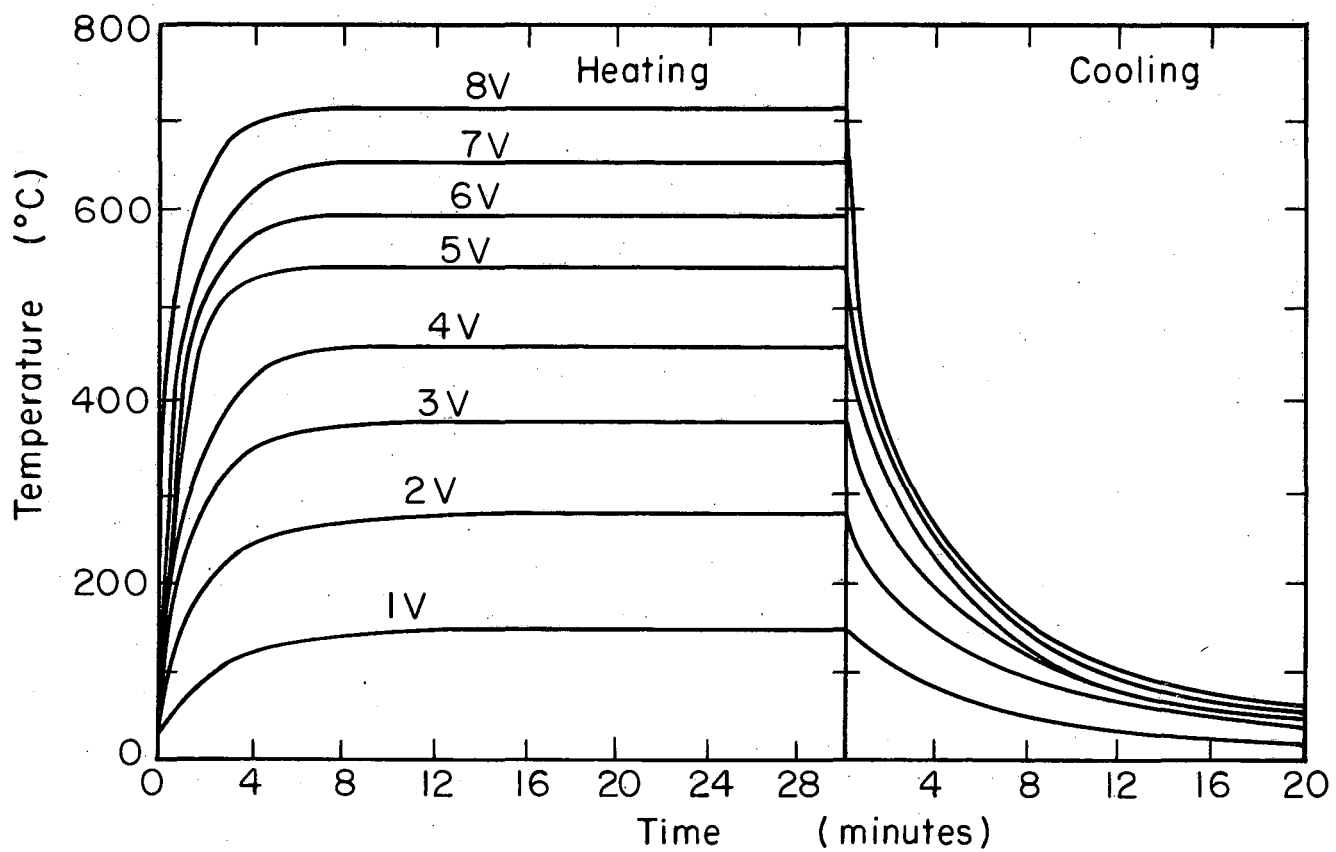
ZN-4937

Fig. 2



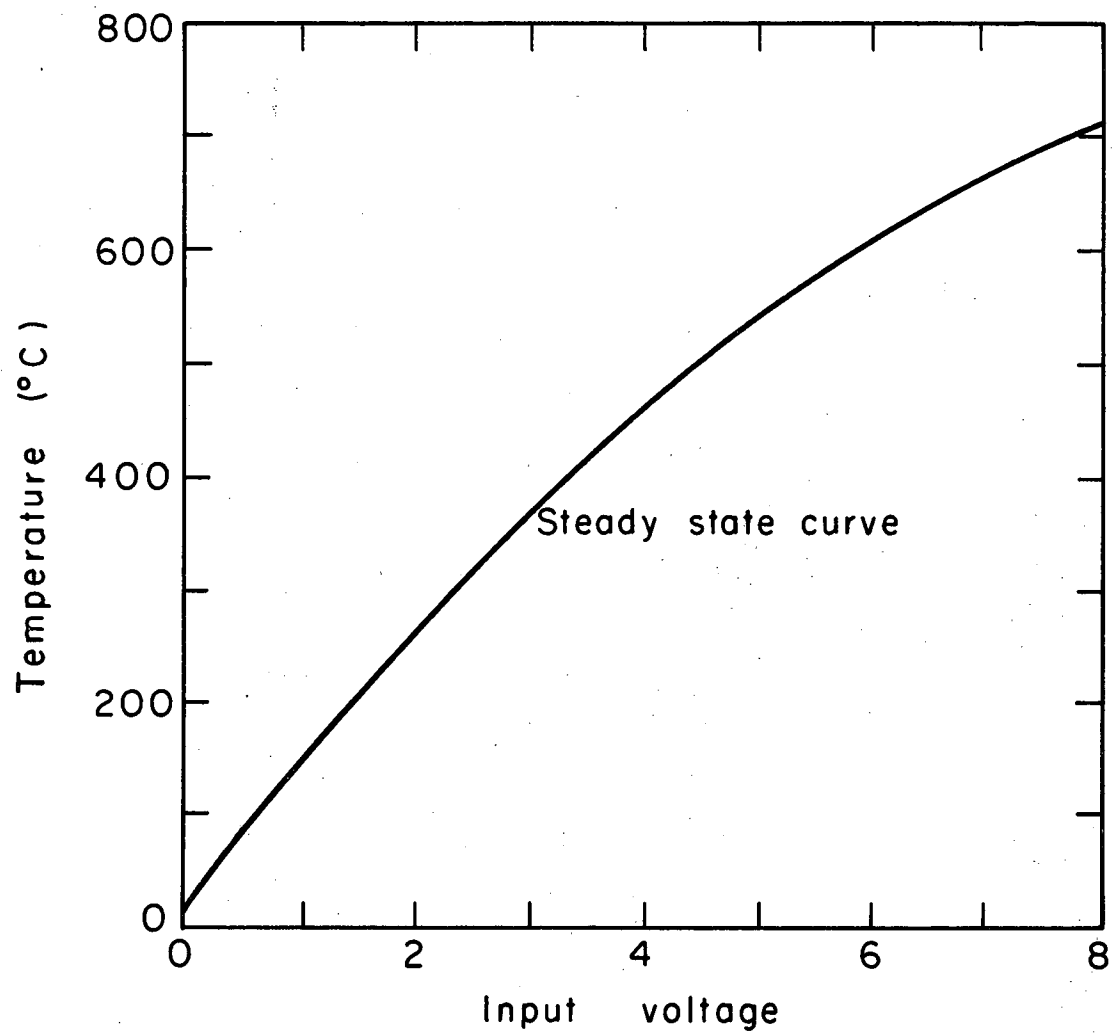
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Fig. 3



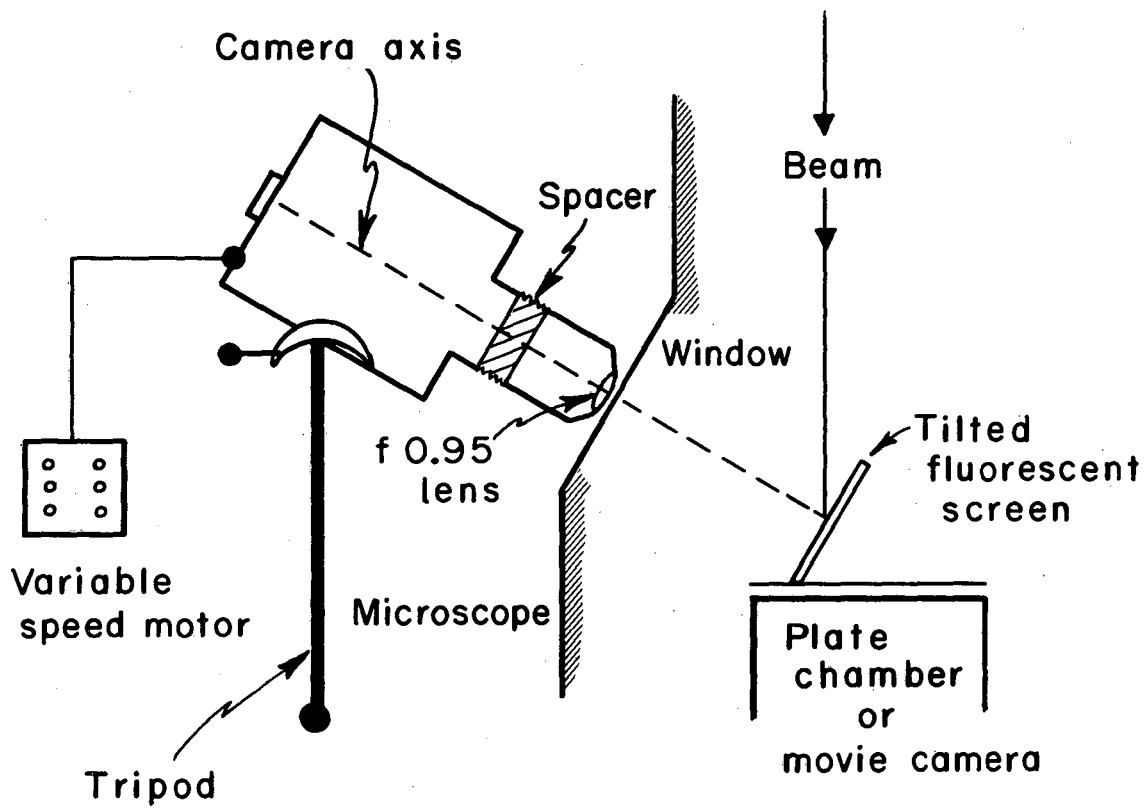
MUB-5170

Fig. 4(a)



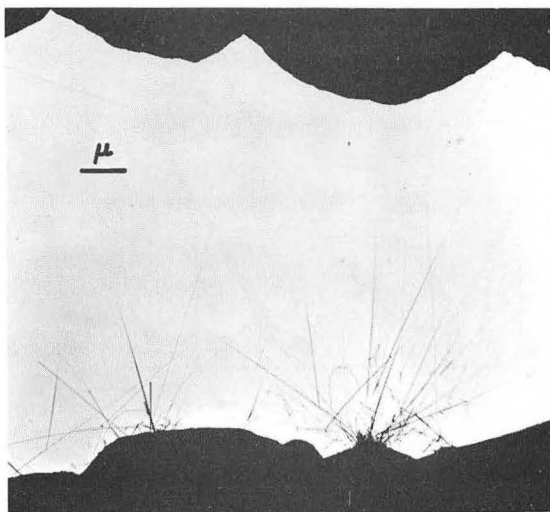
MUB-5172

Fig. 4(b)



MUB-5116

Fig. 5



a

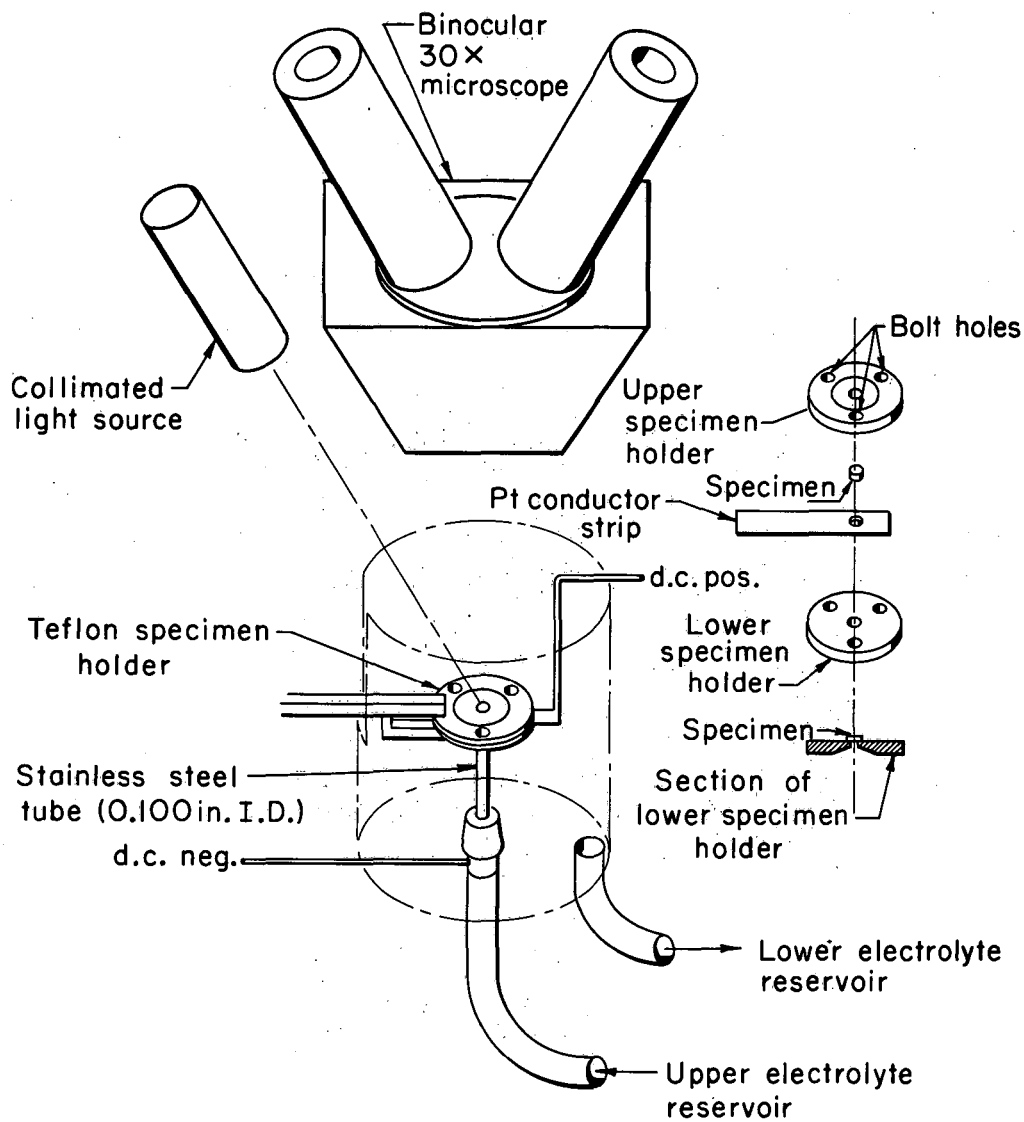


b

ZN-4756

Fig. 6

Micro-Electropolish Arrangement



MUB-4449

Fig. 7

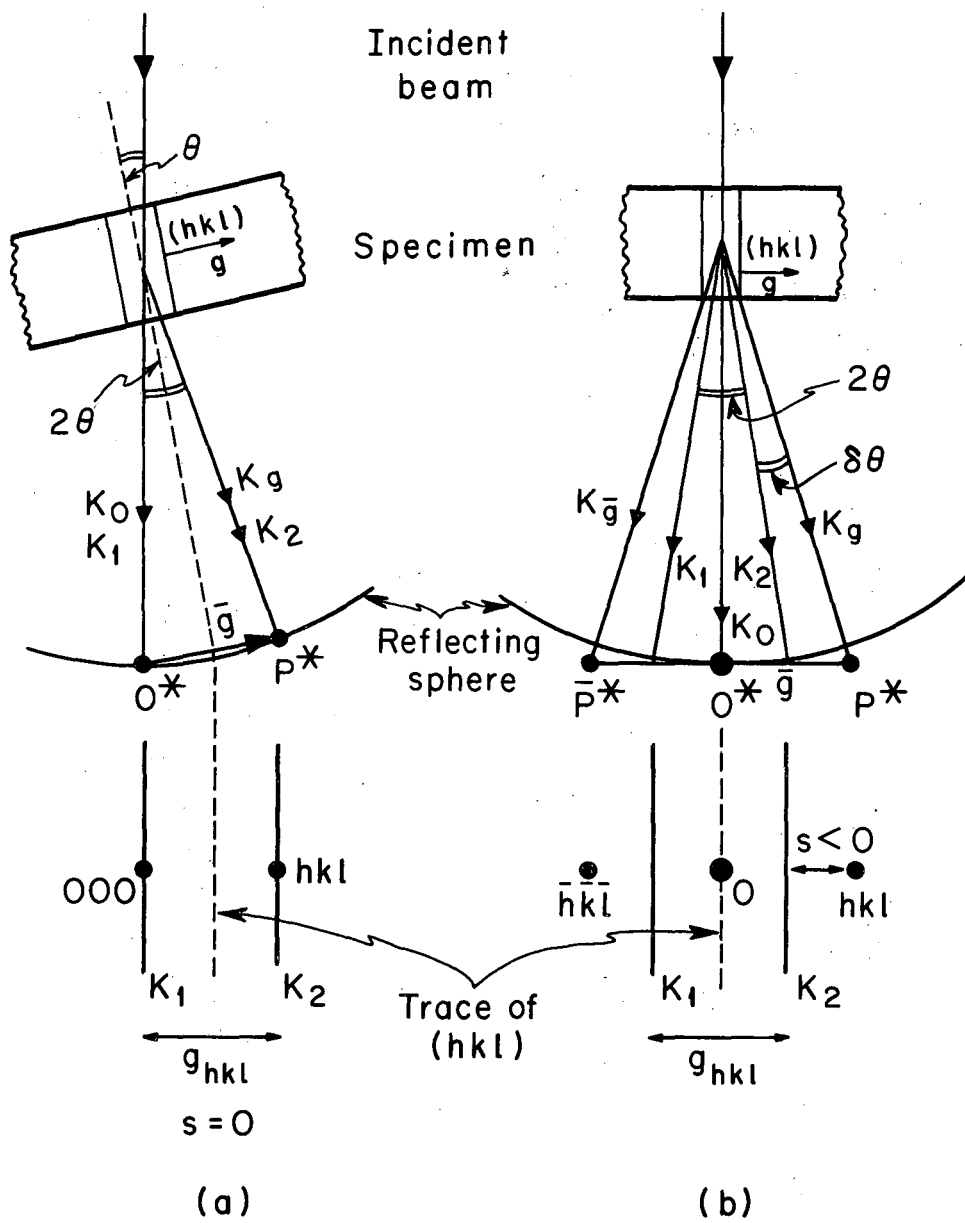
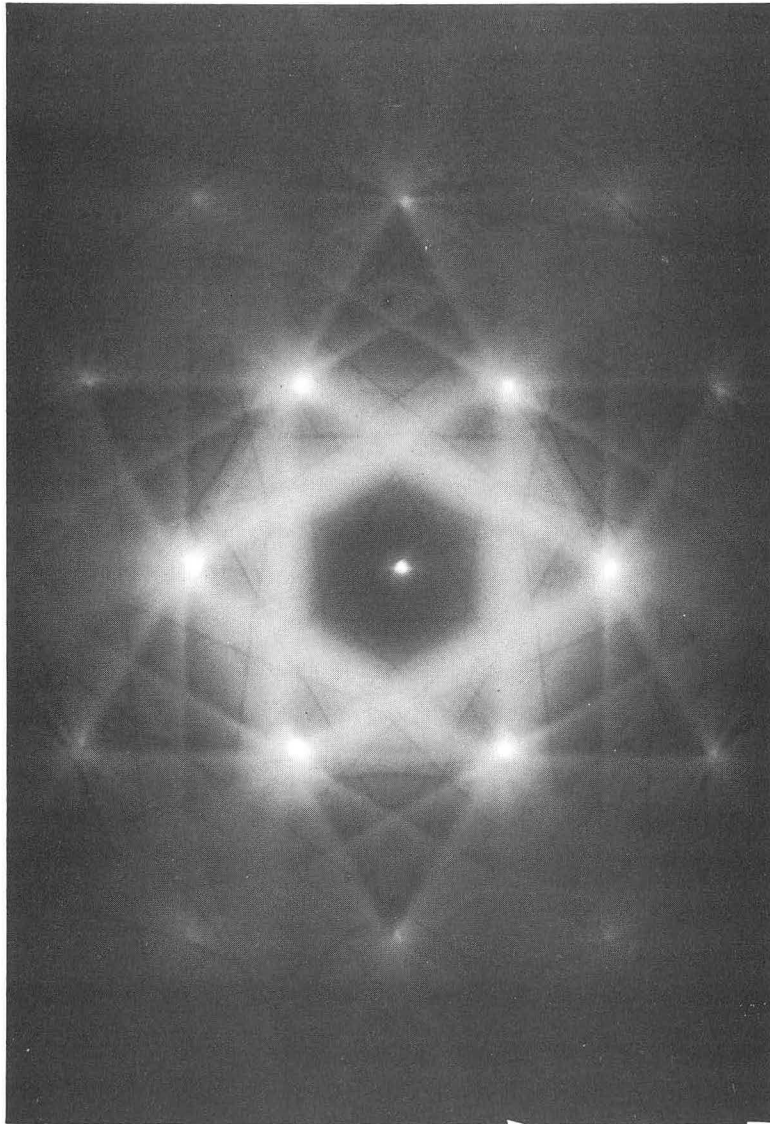


Fig. 8

MUB-4501



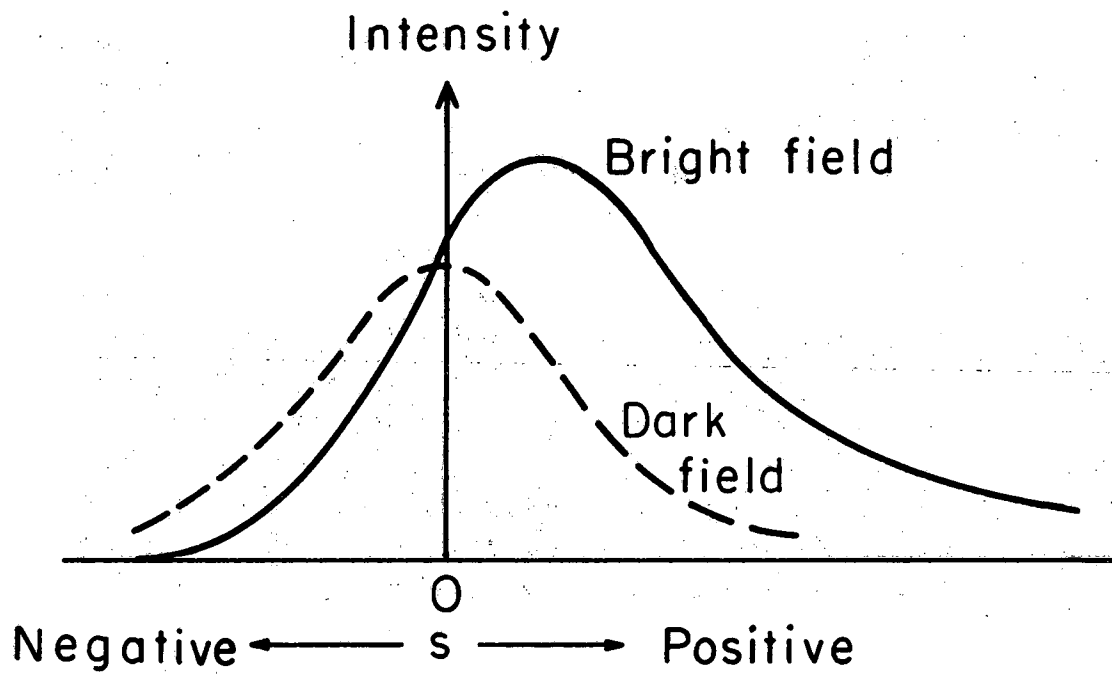
ZN-4938

Fig. 9



ZN-4963

Fig. 10



MUB-5173

Fig. 11

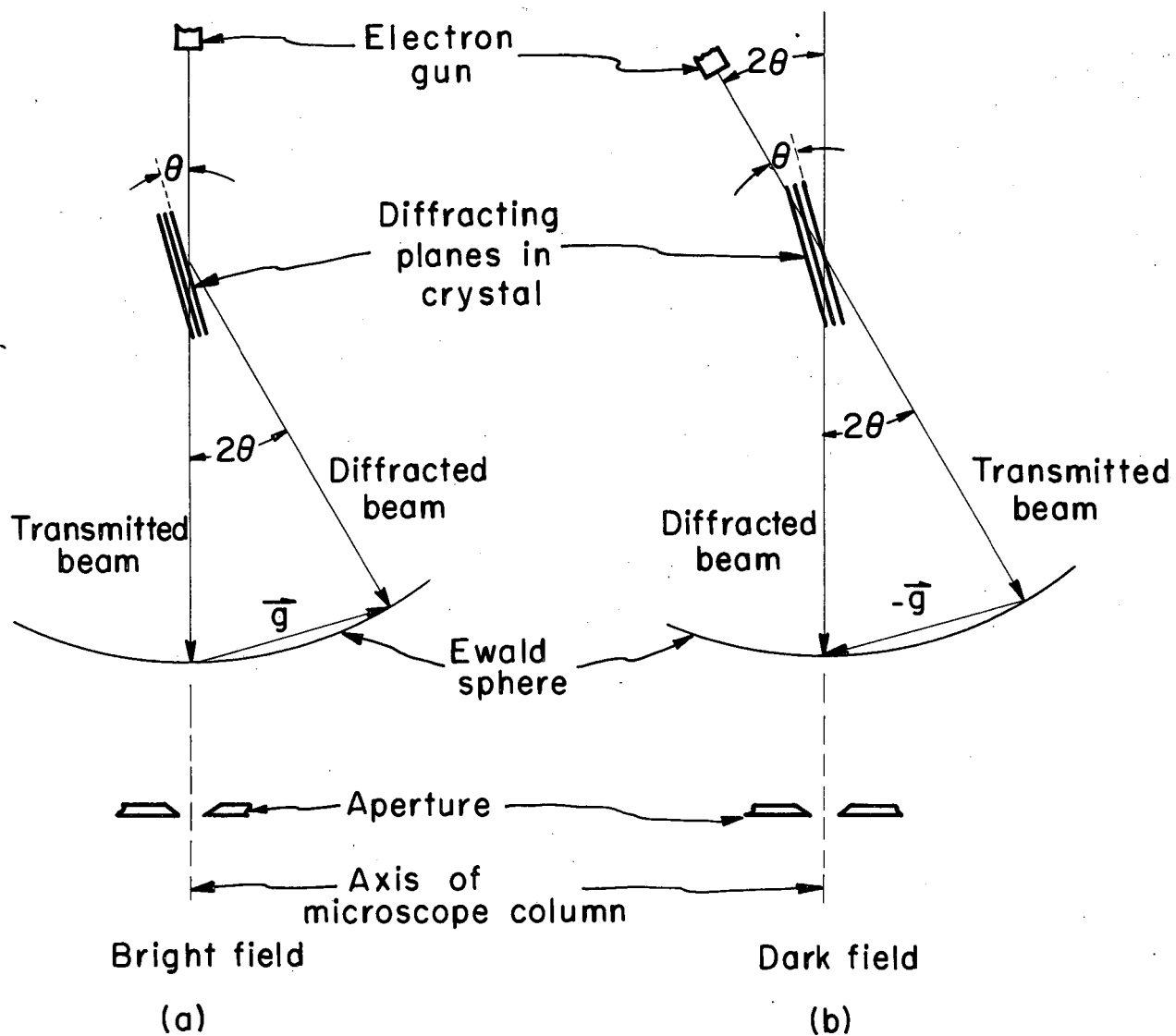
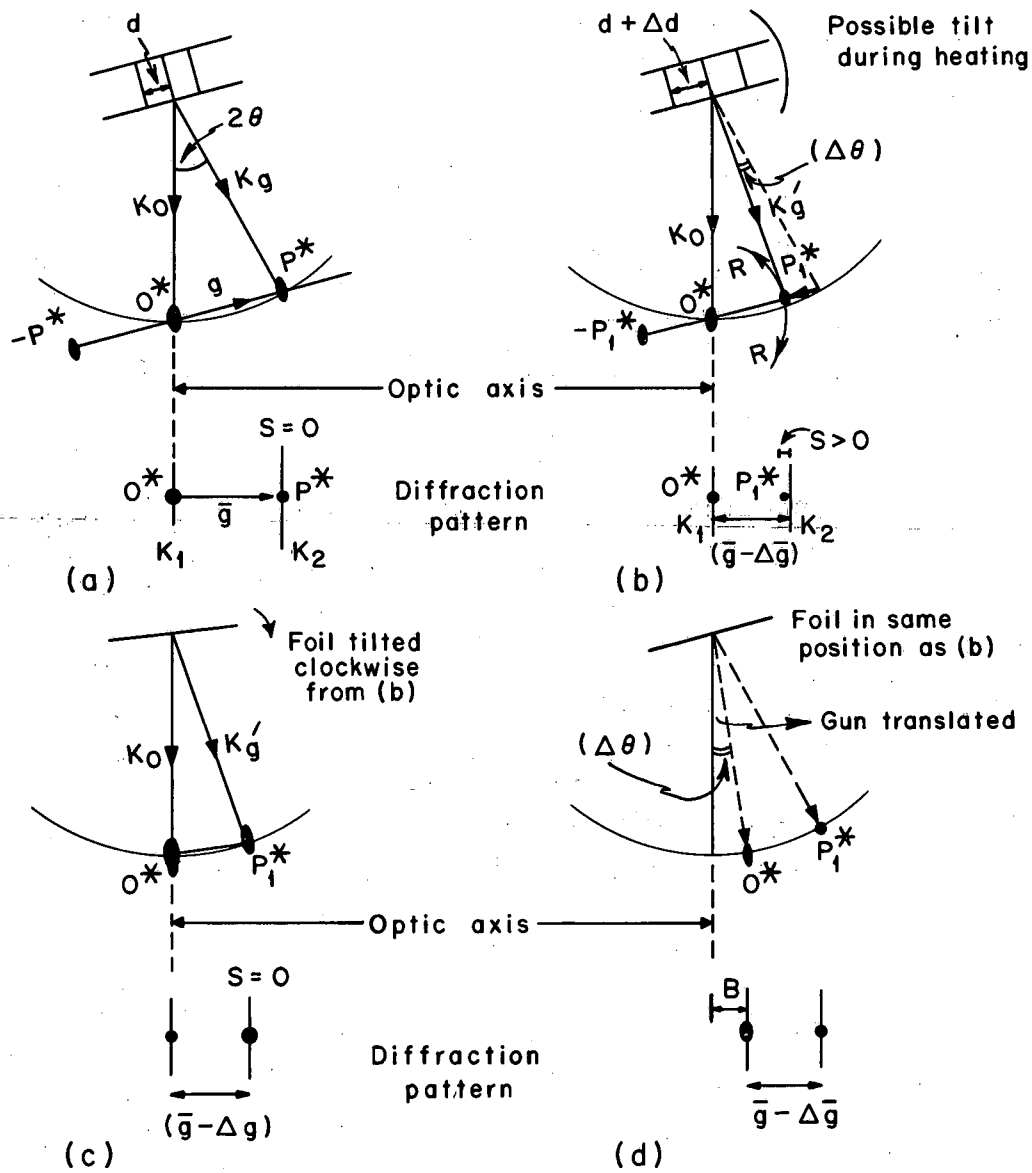


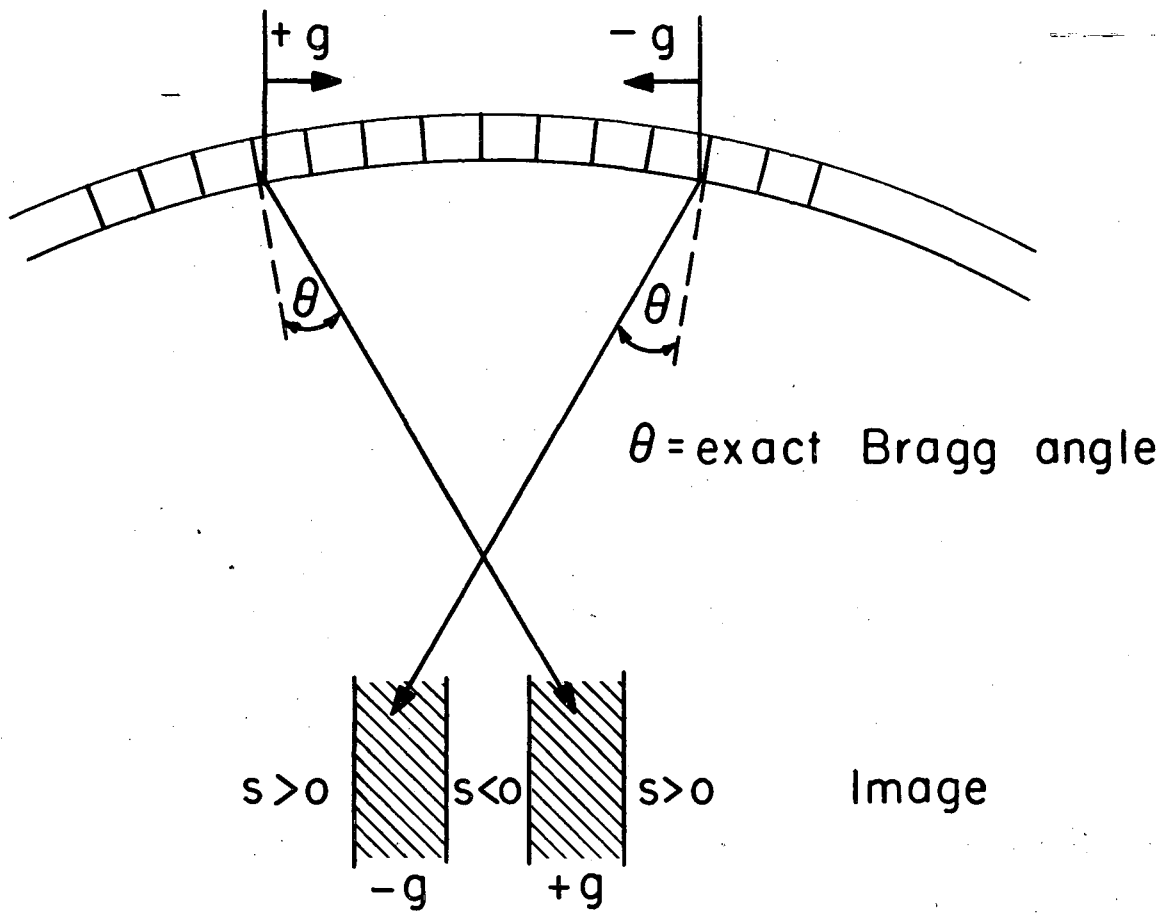
Fig. 12

MUB-3766



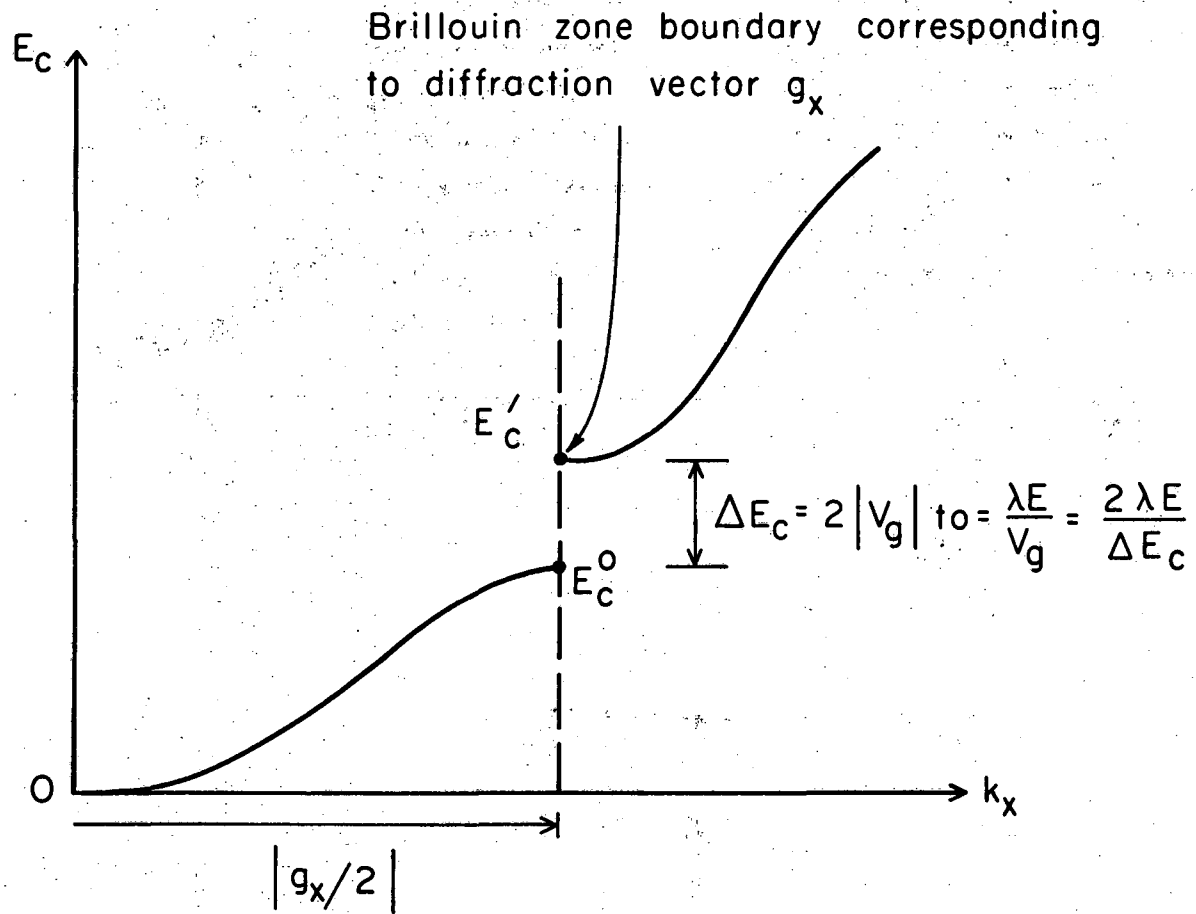
MUB-5117

Fig. 13



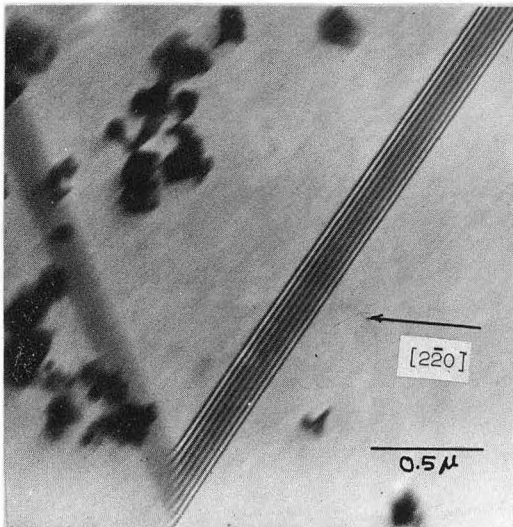
MUB-5169

Fig. 14

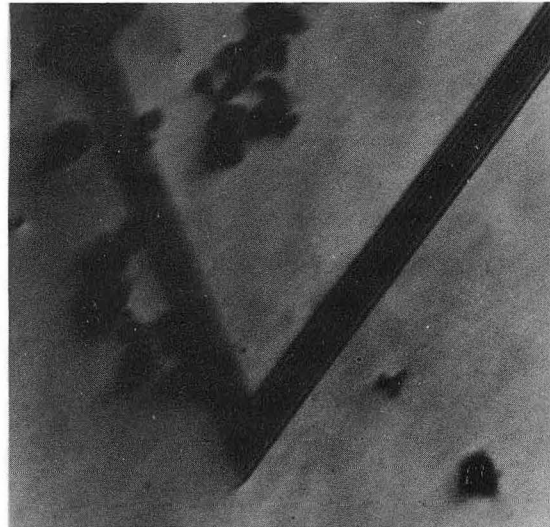


MUB-5167

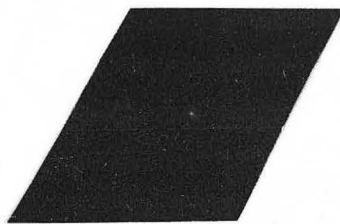
Fig. 15



(a)

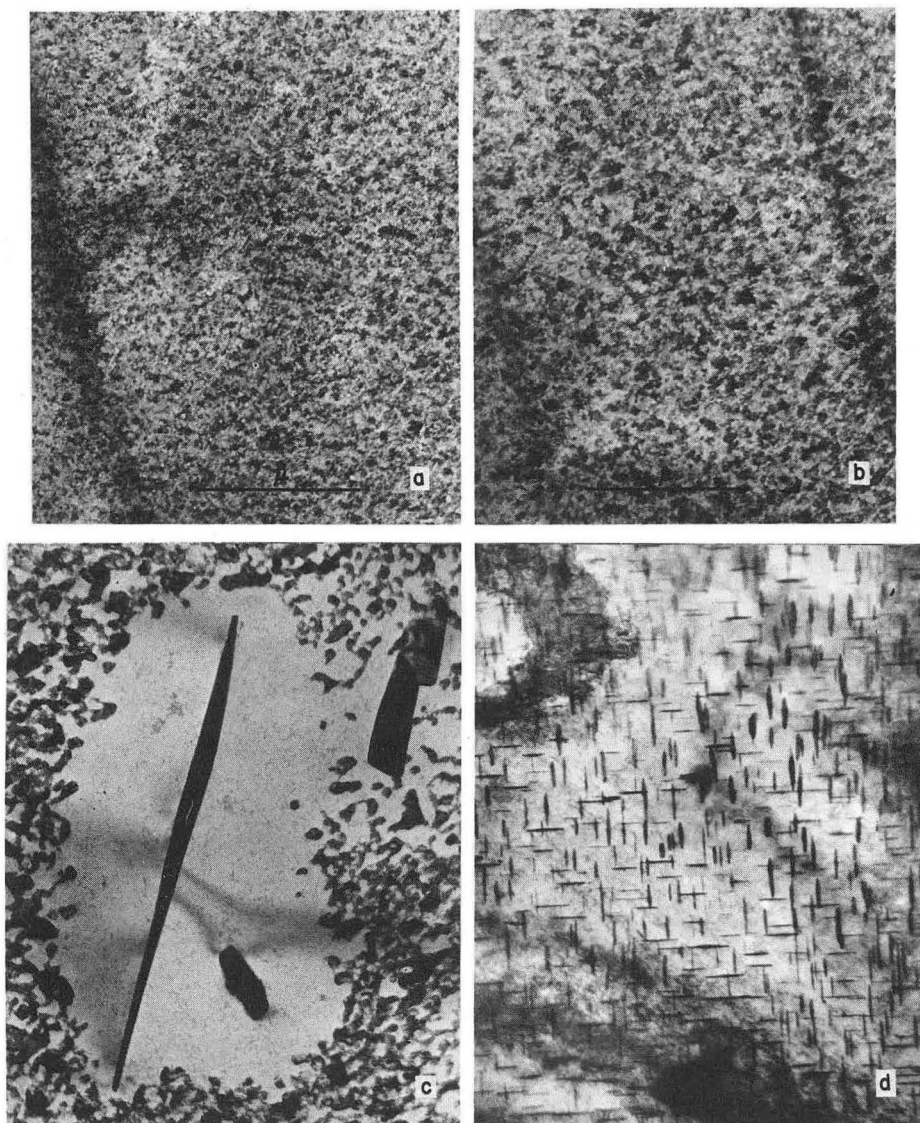


(b)



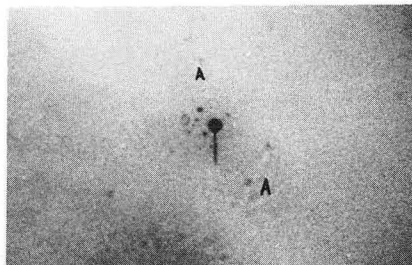
ZN-4913

Fig. 16 a, b

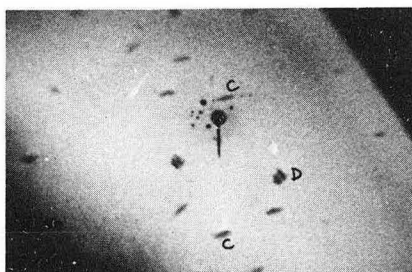


ZN-4759

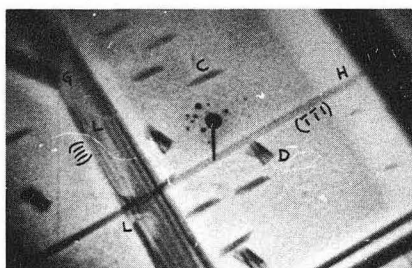
Fig. 17 a, b



a



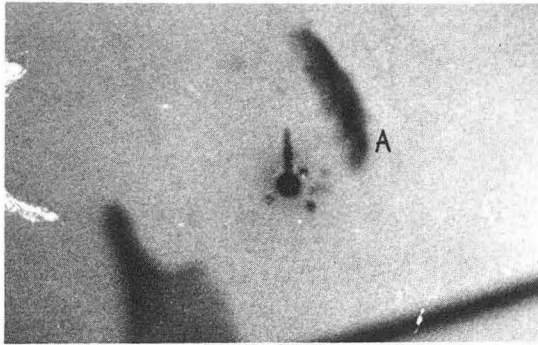
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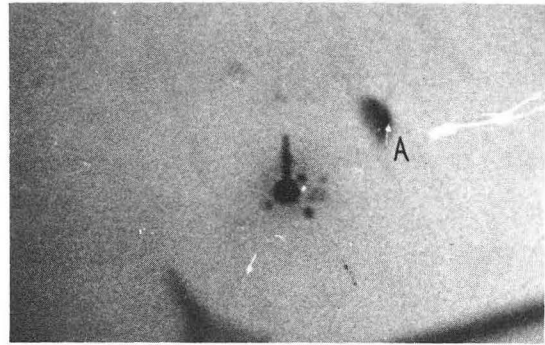
c

ZN-4910

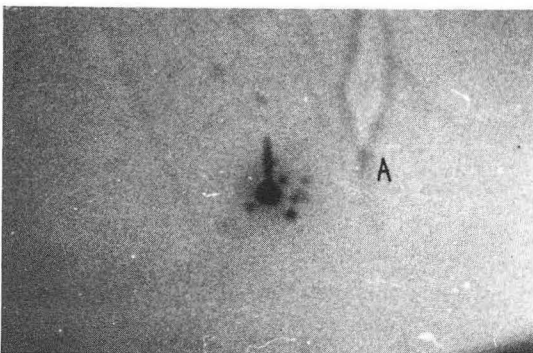
Fig. 18



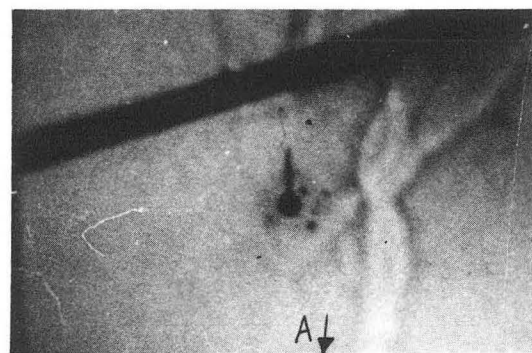
a



b



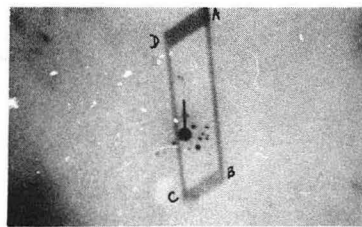
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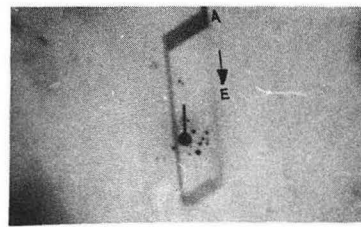
d

ZN-4911

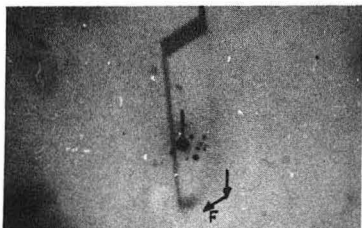
Fig. 19



a



b



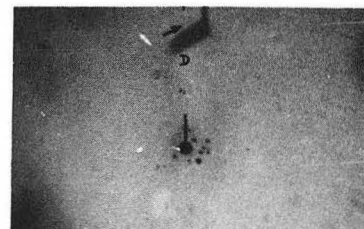
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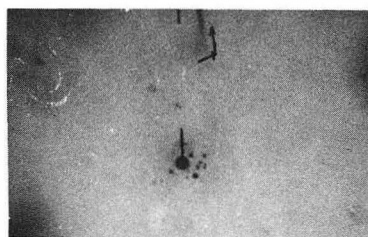
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e



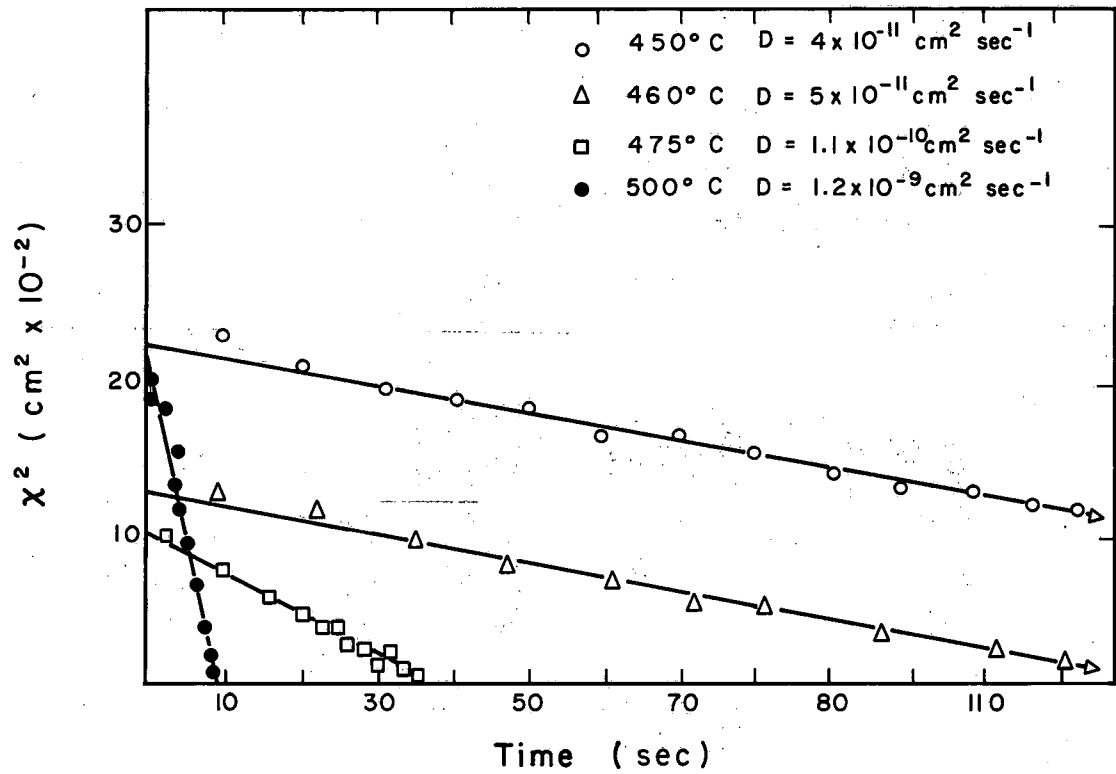
f



g

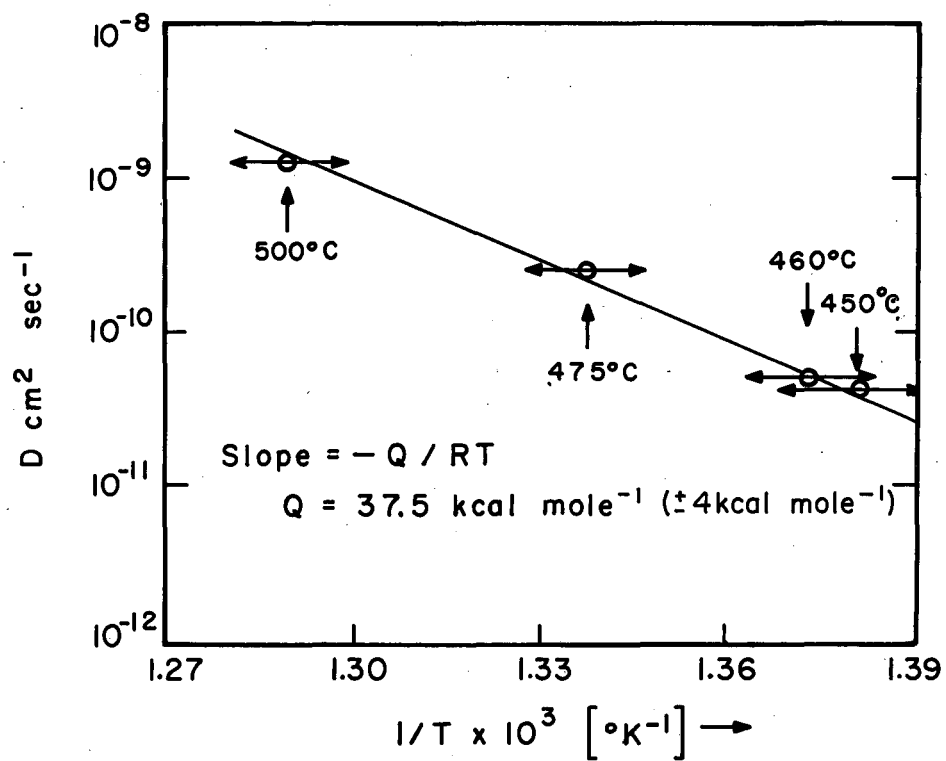
ZN-4912

Fig. 20



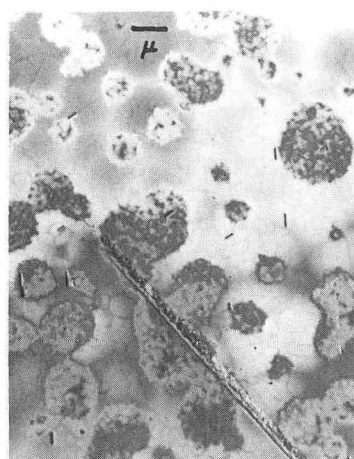
MU-26033

Fig. 21(a)

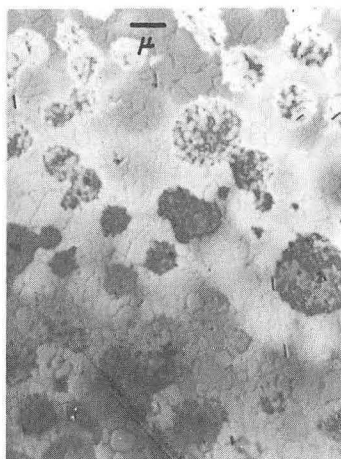


MU-26034

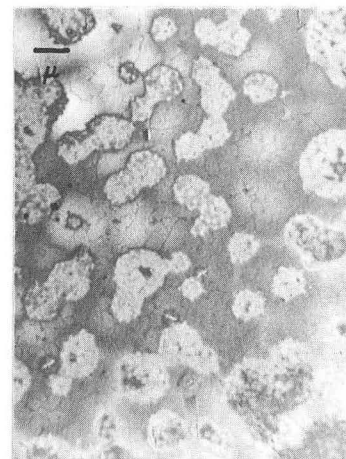
Fig. 21(b)



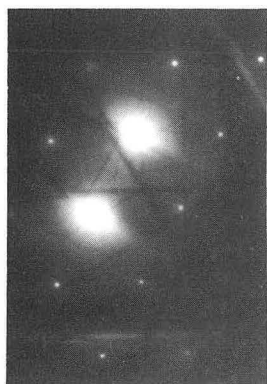
a



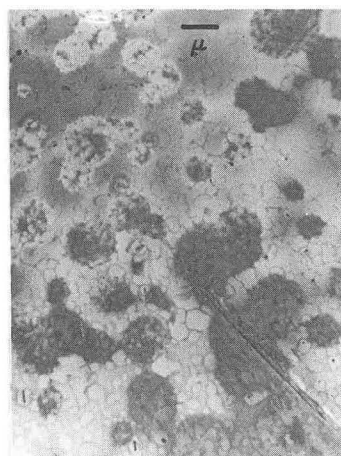
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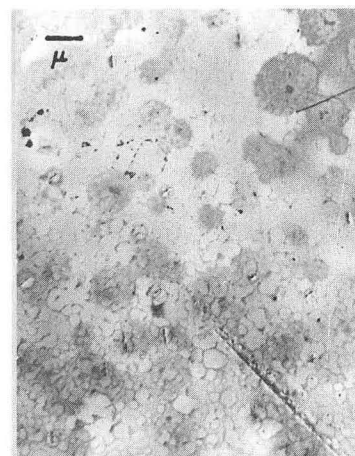
c



d



e



f

ZN-4752

Fig. 22



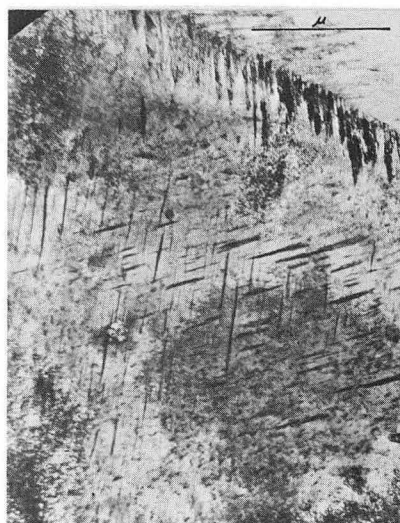
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b



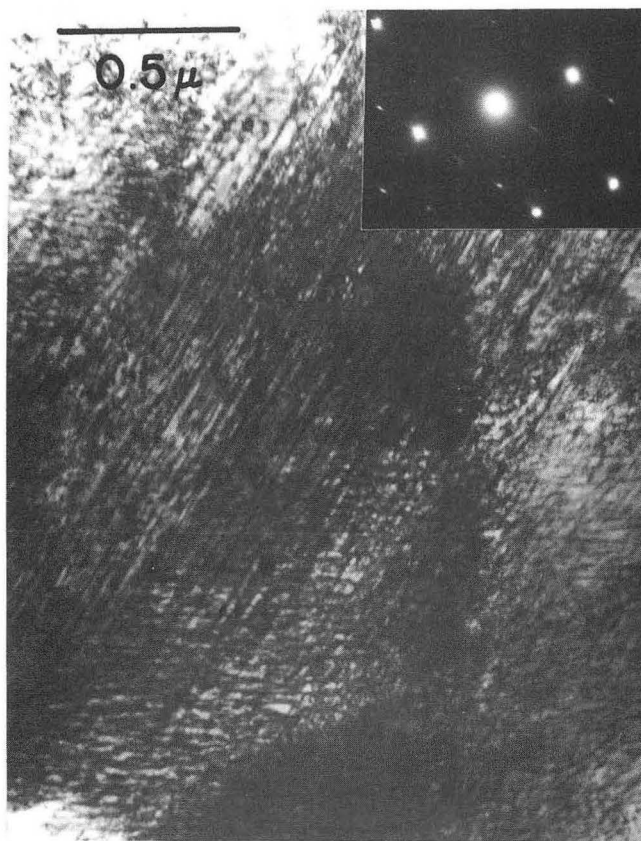
c



d

ZN-4689

Fig. 23



ZN-4690

Fig. 24



a

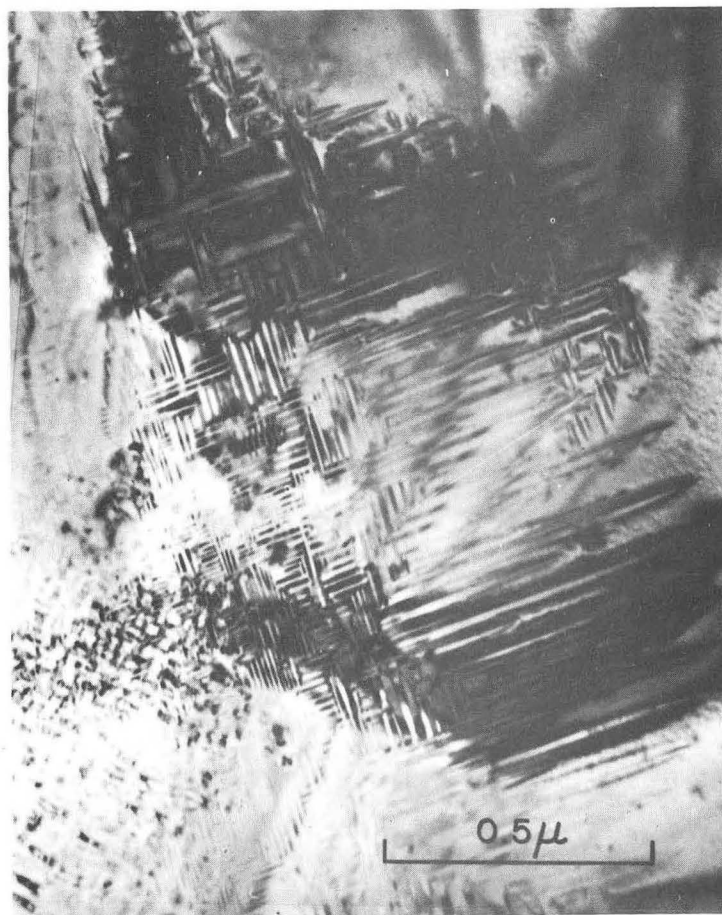


b



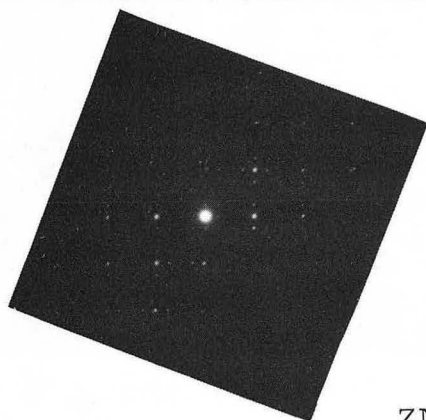
ZN-4687

Fig. 25



ZN-4964

Fig. 26(a)



ZN-4668

Fig. 26(b)

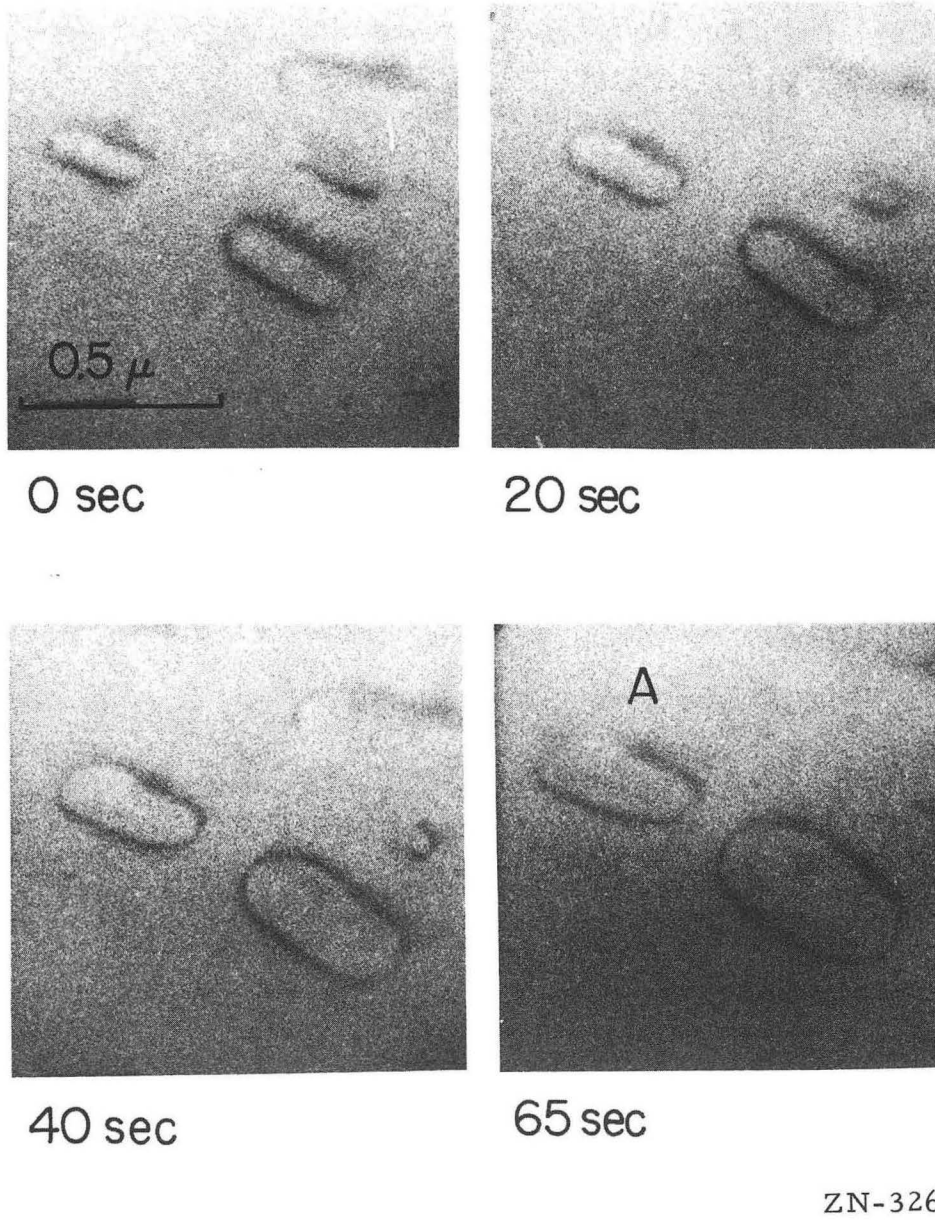
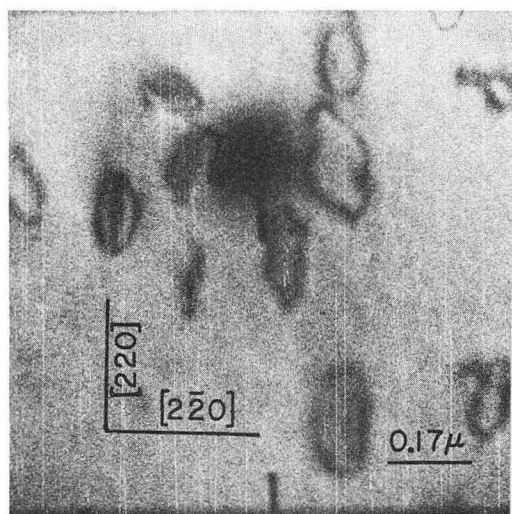
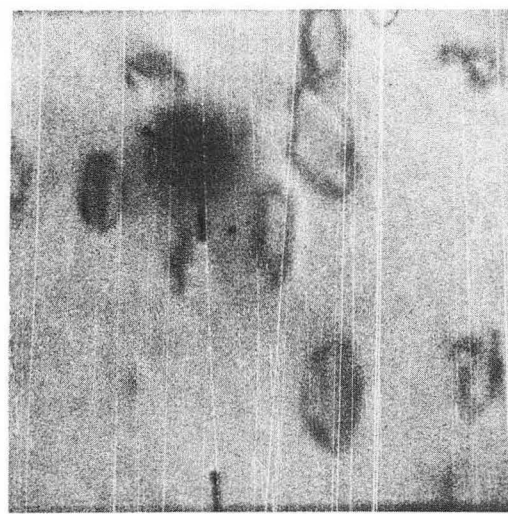


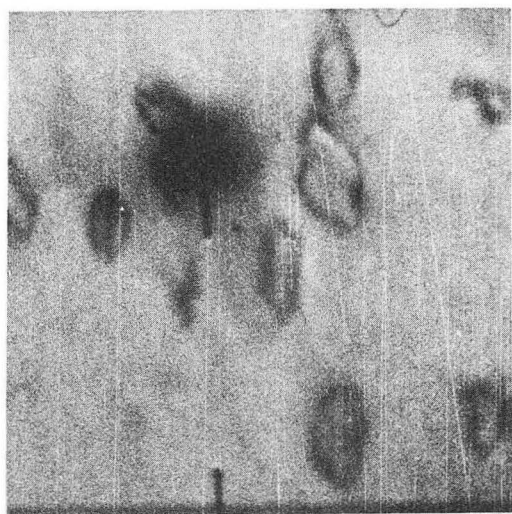
Fig. 26



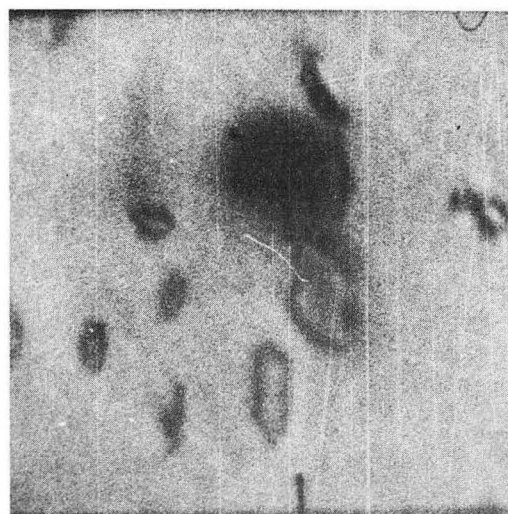
(a) 0



(b) 17



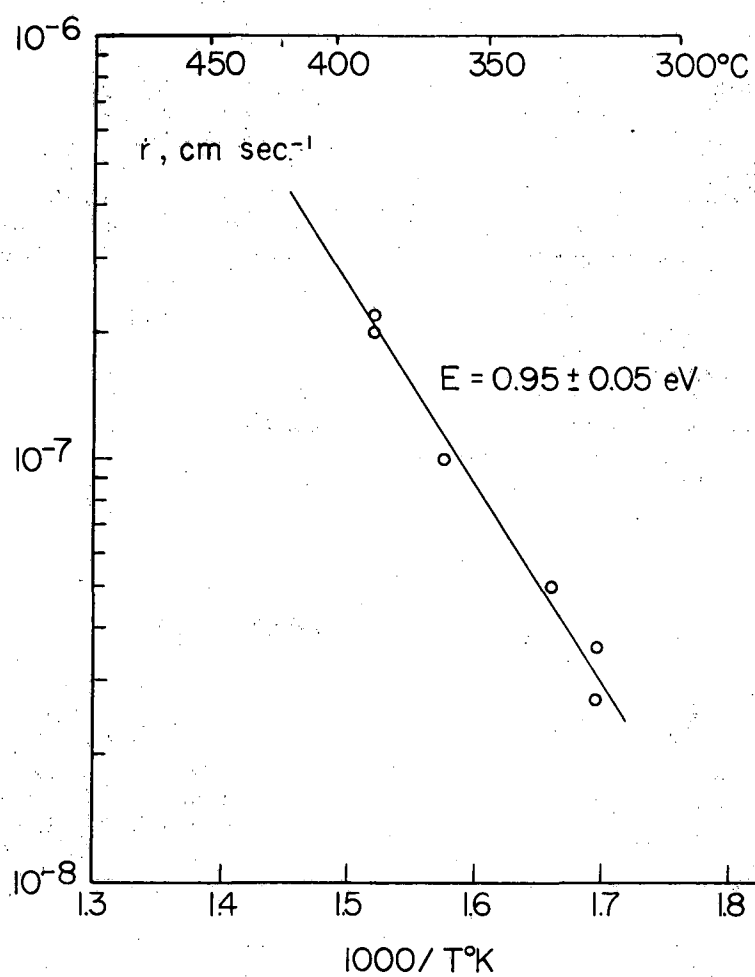
(c) 33



(d) 50

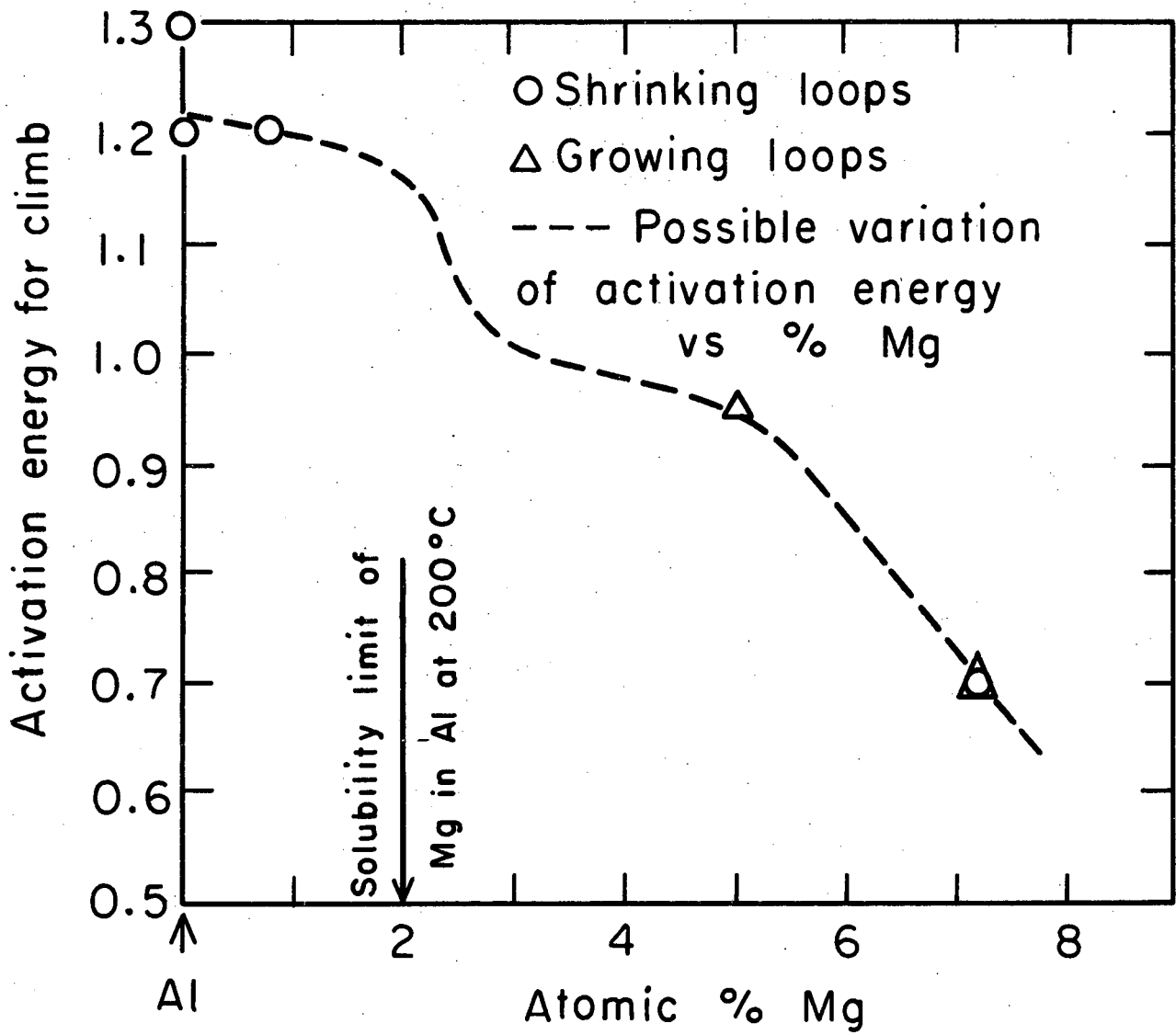
ZN-4819

Fig. 28



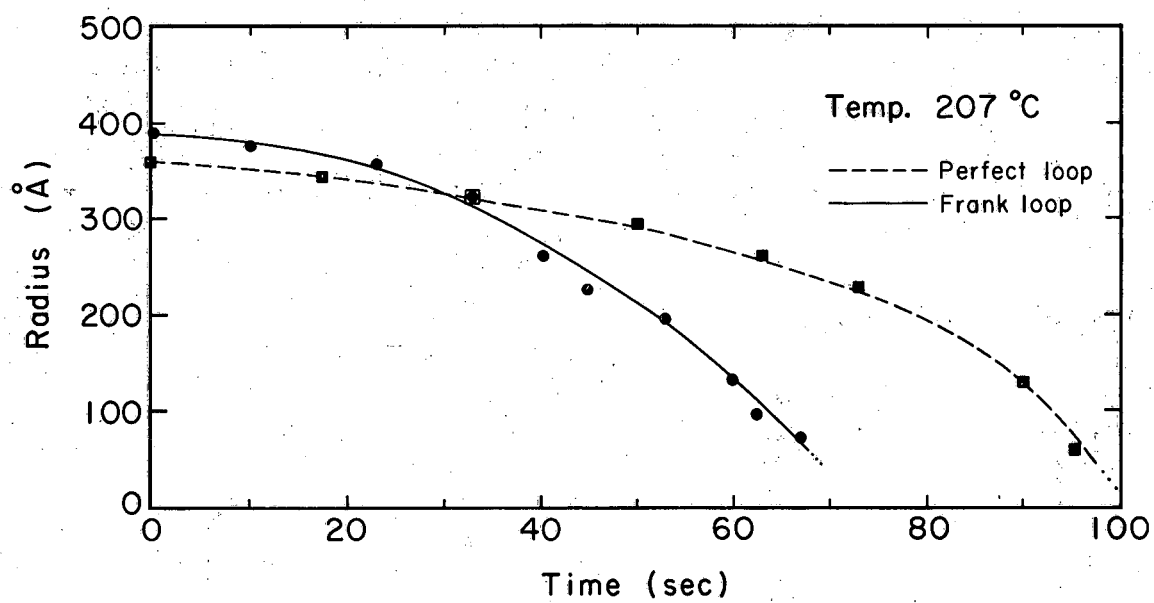
MU-27667

Fig. 29



MUB-5171

Fig. 30



MU-35239

Fig. 31

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