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# Rensselaer Polytechnic Institute

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# Materials Research

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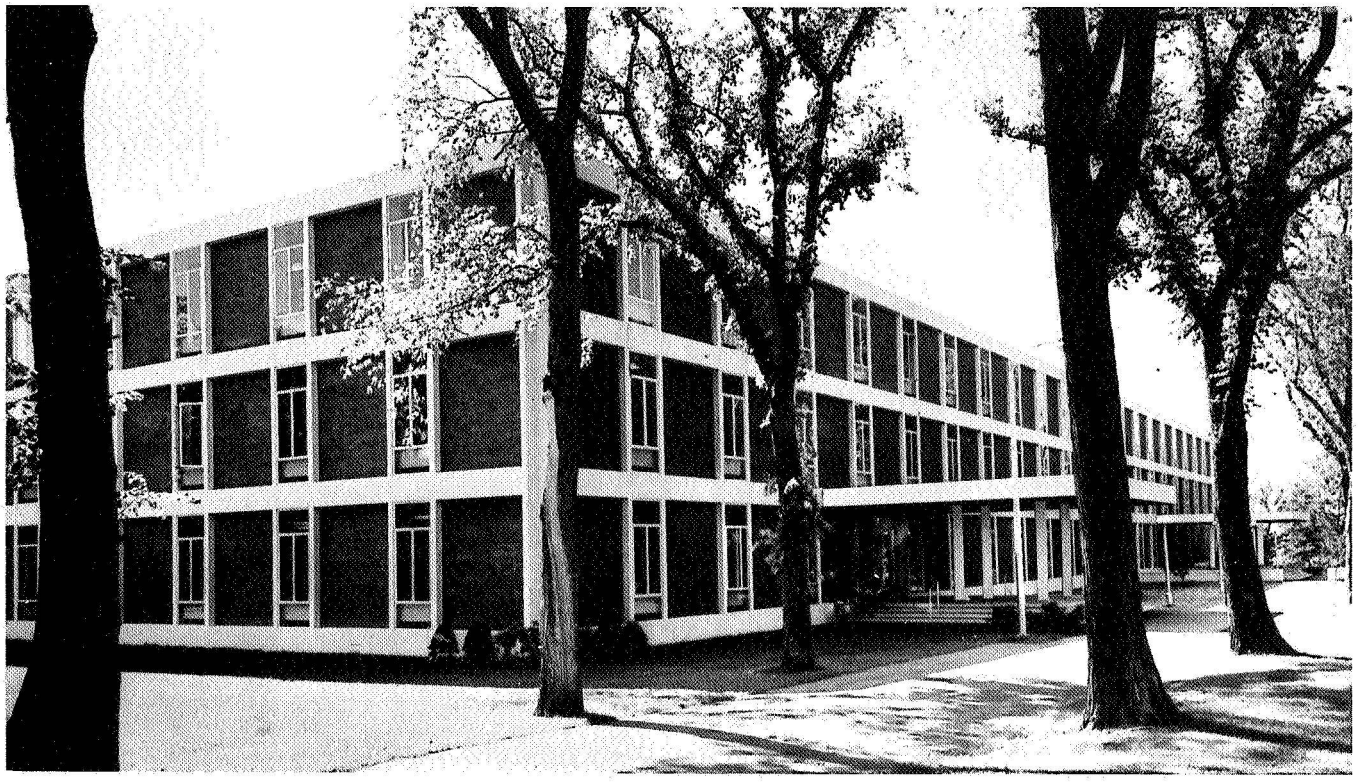

# SEMI-ANNUAL PROGRESS REPORT

## NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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Rensselaer Polytechnic Institute
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Rensselaer Polytechnic Institute
Troy, New York

Semi-Annual Progress Report
National Aeronautics and Space Administration Grant NGL-33-018-003
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## INTRODUCTION

Rensselaer Polytechnic Institute's Materials Research Center was established in 1960 when NASA awarded the university a continuing grant to support research in the materials area. Since that time the program has provided support for research projects which have helped to educate over 225 graduate students.

The output from the program over the years in the form of technical papers submitted for publication has increased annually. Since the program's inception, a total of 144 technical papers have been submitted for publication. It is interesting to note that of these 144 publications over 1/3 (51) have been submitted during the last 12 months. From this aspect, it would appear that the program is reaching a mature stage that will in the future greatly add to the fund of knowledge in the materials area.

This sixteenth semi-annual summary report follows the same format as the previous report with the emphasis on function rather than on discipline. It is again divided into five sections, each preceded by a semi-technical introduction which gives a broad picture of the research going on in that particular area. These introductions are followed by more technical write-ups of the research being conducted. The five areas are: Structural Characterization and Synthesis, Solid State Reactions and Phase Transformations, Mechanical Properties and Strengthening Mechanisms, Electronic and Thermal Properties, and Environment-Sensitive Behavior.

# STRUCTURAL CHARACTERIZATION AND SYNTHESIS

# STRUCTURAL CHARACTERIZATION AND SYNTHESIS

In reviewing the project reports in the areas of the synthesis of new materials and the structural characterization of both old and new compounds, one cannot but remark on the wide variety of systems studied, the number of physical techniques utilized, and the importance of polymers to this aspect of Rensselaer's materials program.

Almost every major class of chemical substances is represented in the studies reported in this section, ranging from metals and alloys through inorganic salts, ceramics, and glasses, to organic high polymers. Analysis and characterization techniques include x-ray diffraction, nuclear magnetic resonance and electron spin resonance, light scattering, permeation chromatography, vapor sorption, dilatometry, calorimetry, and radiotracer techniques.

Several projects, including those on amorphous films, selenium-based glasses, and polymerization kinetics, have either terminated or are in their final stages. Others, including studies of boron monofilaments, and of dispersion in gel permeation chromatography, have produced results of unusual interest in the past reporting period. Some highlights of these projects are summarized here:

We have produced high strength (300,000 - 360,000 psi) boron monofilaments using potentially low-cost carbon monofilaments in place of expensive, dense tungsten filaments as the substrate.

Our theory of dispersion in gel permeation chromatography has been applied with great success to columns packed with porous glass beads and with crosslinked polystyrene gels. Since the effects of free-stream dispersion (outside the gel) are well known as the result of our previous

work with non-porous glass beads, their contribution to the total dispersion in the two porous systems could be evaluated. The predominant factors causing dispersion with the polystyrene column-packing materials were found to be mobile-phase effects occurring outside the gel, while with the glass beads, dispersion was caused primarily by permeation or mass-transfer effects. These results correlate nicely with differences in the structure of the two substrates.

Our studies of the kinetics of the photopolymerization of methyl methacrylate have led to the apparently contradictory, but in fact logical, conclusion that the way to achieve complete polymerization most rapidly is to start the reaction under conditions of low, rather than high initial rate.

## AMORPHOUS FILMS

Senior Investigator: J. D. Mackenzie

Amorphous films are becoming increasingly important in the electronic industry. Our work has been concentrated on the preparation of (a) new insulating films and (b) new conductive films. Under (a), studies on amorphous silicon nitride films have been continued. The effects of non-stoichiometry on properties have been studied. The relationships between these non-crystalline films and their crystalline compounds are also being examined. Under (b), work has been concentrated on iron oxide, nickel oxide and iron-nickel-oxide films. The electronic and optical properties of these films are being studied. These two projects should be completed in the next period.

## SELENIUM-BASED GLASSES

Senior Investigator: J. D. Mackenzie

Glassy selenium is a well-known photoconductor. Its conductivity is very low. Our work has been concentrated on the structural characterization by infrared absorption of glassy selenium containing impurities such as oxygen, silicon and mercury. Such impurities have extremely large effects on the electrical properties of the glass.

## THE RELATION OF DEPOSITION CONDITIONS TO STRUCTURE IN PYROLYTIC CARBONS

Senior Investigator: R. J. Diefendorf

The properties and structure of pyrolytic graphite have been reported by many investigators. The data often seem inconsistent and

contradictory. The reasons for this apparent inconsistency include incomplete specification of all the deposition variables, so that exact duplication is impossible. It was the purpose of this investigation to examine the structure of pyrolytic graphite and relate it to the deposition conditions and observed properties.

A large number of pyrolytic carbons was made over a wide range of conditions in ½" diameter tubes 8" long. Optical, electronoptical, and x-ray diffraction were employed to determine structure. Density and residual stress measurements were also performed.

The interpretation of the results is conceptually simplified if deposition is described in terms of depositing specie, rate of deposition, and surface mobility. The last two terms essentially define a nucleation rate. An increase in density occurs with the breakdown of methane to the high temperature stable species of H, $H_2$, $C_2H$ and $C_2H_2$. Higher wall temperatures give higher densities when deposition is from the high temperature stable species. Higher flow rate increases deposition rate by improved mass transfer, and slightly lower densities are observed. The exact density depends on how fast carbon can rearrange on the surface. Nucleation of growth cones also follows the ratio of deposition rate/surface mobility. Higher pressures and flow rates and lower temperatures favor high nucleation rates and lower densities. All the densities are relatively high, and all structures are deposited from small species, probably $C_2H$ or $C_3H$. The low-density deposits often reported in the 1500°C to 1700°C range are not formed by deposition from small species. These deposits are formed at sufficiently high supersaturations that gas phase soot nucleation occurs and soot particles are then trapped into the

structure. Low-density deposits may result under sooting conditions or when deposition occurs from some primary fragment of methane.

The nucleation of growth cones in the deposit decreases from the inlet to exit of the deposition tube because of carbon depletion in the gas in non-sooting runs. When soot formation occurs, the nucleation rate may increase with distance from the inlet, since the formation of soot takes time. If the formation of the soot is sufficiently slow, the nucleation rate may drop off due to carbon depletion and then build up because of growth cone formation on soot particles.

## THE CHEMICAL VAPOR DEPOSITION OF BORON ON CARBON MONOFILAMENT

Senior Investigator: R. J. Diefendorf

High-strength high-modulus boron filament is made by the hydrogen reduction of boron trichloride on a heated tungsten filament. Although the electrical and mechanical properties of the tungsten are excellent, it is expensive, very dense, and unavailable in large quantities. The recent development of a high-strength uniform-carbon monofilament with potentially low cost offers an alternate substrate for the halide process.

Early studies with carbon monofilament by the boron filament producers gave extremely poor results. Although the electrical resistance of the carbon monofilament was more uniform than that of the original tungsten, hot spots appeared along the filament during processing. The cause of the hot spots was found to be fracturing of the substrate. The substrate core was boriding after an outer shell of boron had formed on it. The shrinkage of the core upon boriding placed the core under tension, and fracture occurred.

When conditions were changed to eliminate hot spots, reactor stability problems were encountered. These were controlled sufficiently to produce high-strength boron filament with a carbon monofilament substrate. The filament is visually similar to boron on tungsten and strengths have averaged around 300,000 p.s.i., with selected runs as high as 360,000 p.s.i. Recently, WPAFB has awarded a contract to AVCO-RPI-GREAT LAKES to develop the process further.

## X-RAY SCATTERING

Senior Investigator: J. L. Katz

Principal emphasis in these studies has continued to be the correlation between the structure of materials and their behavior and function.

Preliminary studies on single crystals of mercury are in progress in order to obtain the necessary orientations for use in a study of the temperature dependence of the thermal vibrations. This will make use of the liquid helium x-ray cryostat and cover the range from about 4.5K to just below the melting point of Hg.

The theoretical study of integrated x-ray intensities for zinc has been completed with the calculation and comparison of the acoustic and optic mode contributions for several reflections. In addition, the behavior of the thermal diffuse x-ray scattering (T.D.S.) near a systematic absence has been calculated. Similar techniques will be utilized in the Hg study based on x-ray measurements as well as on the elastic constant measurements made by Dr. Salinger's group.

Studies on the elastic properties of amalgams have been continued

with investigation of the temperature and pressure dependent behavior of the individual phases. This work is being correlated with the study of the $\gamma_2$ (tin-mercury) phase disappearance in order to explain the composite behavior of amalgam.

Another area of continued interest in the behavior of composite materials has been in hard tissue (bone and teeth). The elastic moduli of hydroxy-, fluor-, and chlor- apatites have been measured by ultrasonic techniques as a function of pressure. In addition, an $NaClCa_5(PO_4)_3 \cdot OH$ composite was similarly measured. The composite behavior observed here was used as a model to initiate a similar two-phase composite calculation for hard tissue based on collagen and hydroxyapatite. The results were reported in an invited paper to the "International Symposium on Structural Properties of Hydroxyapatite and Related Compounds," held at the National Bureau of Standards.

These studies on the composite nature of hard tissue are being used as the basis for a corollary study on the design of materials for prosthetic and restorative purposes.

## SOLID STATE AND PHASE STUDIES OF INORGANIC MATERIALS

Senior Investigator: H. Wiedemeier

The objectives of this work are to investigate structural properties of inorganic compounds and phase relationships of mixed systems. Both aspects are important for the understanding of solid state reactions and for the synthesis of new materials.

Recent investigations in our laboratory of the phase diagram of the MnS-MnSe system by vapor-transport techniques revealed solid solution over the entire range of composition and the formation of

single mixed crystals in this system. This led to systematic studies of single-crystal growth and transport properties of an alloy system which are presently being carried out.

For this purpose the alloy $MnS_{0.5}Se_{0.5}$ was chosen for chemical transport reactions with iodine as a transport agent. The system MnS-MnSe-iodine represents a multi-component multi-reaction system. The complexity of this system is furthermore emphasized through the fact that the starting material (mixture of elemental Mn, S, and Se) is different from the final product (solid solution). These are unusual conditions and attempts are being made to deduce the transport mode and mechanism in this system from observation of the transport rate as a function of iodine pressure in the transport tube. It will be very interesting to compare the data with results obtained for simpler systems.

Little is known about the effect of experimental parameters on crystal habit in a vapor-transport reaction. As part of the present work the crystal morphology of MnS, MnSe and $MnS_{0.5}Se_{0.5}$ is being studied under various experimental conditions. This should yield some rules concerning the preferential growth habit of single crystals.

The above studies are being compared to theoretical considerations and will lead to a better understanding of high temperature diffusion and convection phenomena.

## NUCLEAR MAGNETIC RESONANCE FOR THE STRUCTURAL CHARACTERIZATION AND SYNTHESIS

Senior Investigator: P. A. Casabella

The work aimed at understanding the deformability of ions in alkali halides is continuing. In these studies the nuclear magnetic

resonance of one or more of the nuclear species present in the crystal under study is observed as uniaxial pressure is applied to the crystal. The crystals currently being studied are NaF, KBr, and KCl. All measurements of the Na ions in NaF have been completed, and are now being analyzed. A preliminary evaluation indicates good agreement with earlier studies of Na ions in NaCl and NaBr, carried out in this laboratory.

The studies of the Br ions in KBr are now in progress. This crystal presents us with a new challenge because the quality of the available crystals is not as high as that of the other crystals studied. As a result these crystals have considerable permanent internal strains due to dislocations and other imperfections. Thus, to get observable ion deformations much higher pressures must be applied to these crystals than to the crystals studied earlier, with a resulting plastic deformation. In all previous studies the pressures were confined to the region of elastic deformation, and this is the only type of deformation for which the data can be interpreted. However, even in the plastic region a certain fraction of the deformation is elastic, and it appears to be possible to separate the effects of the two types of deformation on the nuclear magnetic resonances. Therefore, it should still be possible to obtain the desired information from the KBr crystals. This line of study will be continued, and the KCl crystals will be studied.

LOW TEMPERATURE MOTIONS IN POLYMERS

Senior Investigator: P. A. Casabella

The most recent studies in this project have been directed toward

understanding the behavior of the proton spin-lattice relaxation time in several polymers in the liquid-helium temperature range. In the last semi-annual report, the relaxation time was reported to be proportional to a negative power of temperature, and the magnitude of the power was close to 1.5 for all polymers studied. At that time this behavior was believed to be due to molecular vibrations. However, as a result of further studies it now appears that the observed relaxation times are due to impurities when there is only a small amount of molecular motion taking place, and at liquid helium temperatures there is very little molecular motion. It has been suggested that the impurity might be oxygen, and in current studies we are attempting to check this idea, and to remove the impurity if possible. In addition, experiments will soon begin in the temperature range above liquid helium temperatures, from 4.2K on up. In this higher temperature range the molecular motion will increase, and its effect on the relaxation time should be easily detectable.

ELECTRON SPIN RESONANCE

Senior Investigator: A. C. Greene

Magnetic resonance studies have been continued on several alkaline earth powders with emphasis on BaS. These powders become optically and magnetically active by application of shear stresses followed by irradiation in the ultraviolet region. Seven absorption lines arising from hyperfine splitting in the magnetic resonance spectrum have been observed and analyzed with respect to absorption frequencies and intensities. The results indicate that the paramagnetic species arises from an F-center configuration, a single electron at a vacant $S^{2-}$ site. This defect is stable at room

temperature and has high symmetry in the lattice despite the observation that it is apparently stabilized by the applied strain. At the present time combined optical and magnetic annealing measurements are being carried out in hopes of identifying optically active configurations. Attempts are also under way to obtain high-purity single crystals of these materials in order to gain more information on the mechanisms whereby these centers are produced and stabilized.

In conjunction with the study of interstitial complexes in alkali halides, a series of computer programs has been written which simulates the structure of face-centered cubic ionic crystals. These programs are designed for the study of defect strain fields which can be detected using both nuclear and electronic magnetic resonance techniques. The computational model at the present time is capable of calculating the relaxation of 1000 ions surrounding a particular defect complex by means of energy minimization through a truncated iteration process. The number of moveable ions required depends upon the nature of the defect complex and can be expanded readily, although at the expense of increased computer time. The basic programs are readily adapted to the study of various defects such as vacancies, interstitials, and substitutional impurities. A successful program of this kind will be extremely useful for general studies of defects and defect interactions in many types of solids.

## LOW-ANGLE LIGHT SCATTERING STUDIES

Senior Investigator: F. W. Billmeyer, Jr.

Complex and painstaking alignment techniques are required with the Phoenix Precision Instrument Company low-angle light scattering

photometer to obtain the narrow well-defined light beam necessary for particle size studies in the 0.2 - 100μ range. These techniques have now been sufficiently refined that the high optical quality of this beam may be consistently maintained with a minimum of effort. The original instrument design has also been modified to include a facility for changing interference filters without disturbing the alignment.

A number of studies using microbiological particles have been completed:

1. The germination of Bacillus cereus spores is accompanied by a size change and thus the germination rate may be studied by low-angle light scattering. The variation in angular scattering pattern and optical density with time were obtained for various concentrations of germinating agent (a mixture of Inosine and L-$\alpha$-$NH_2$ butyric acid). Size interpretations were initially made by Sloan plots and will be followed by precise calculations using Mie theory.

2. The effect of external osmolarity on cell size was examined by scattering measurements with Serratia marcescens in varying concentrations of sodium chloride solution, using suspensions of the cells treated with formaldehyde as a blank. The results will be correlated with direct measurement of cell volumes in concentrated suspensions.

3. The effect of the relative refractive index on the contribution to the angular scattering pattern of the nucleus and cytoplasm respectively of a cell was studied using Bacillis subtilis and demonstrated that the nucleus could more easily be differentiated in suspensions of high relative refractive index.

Further work in preparation includes the calibration of the instrument to obtain absolute scattering intensities as a preliminary

to a study of the light-scattering from samples of DNA from tumor tissue and ordinary tissue, which has proved intractable using more conventional wide-angle instruments.

DISPERSION IN GEL PERMEATION CHROMATOGRAPHY

Senior Investigator: F. W. Billmeyer, Jr.

A satisfactory mathematical model has been obtained to describe mobile-phase dispersion (outside the gel) in gel permeation chromatography (GPC). The model incorporates molecular diffusion, eddy diffusion, and velocity-profile effects as the major causes of axial dispersion. The theory assumes that the average radial dispersion coefficient varies with the sum of the molecular diffusion and eddy diffusion occurring. This assumption has been shown to be valid over the range of flow rates studied, using existing data in the literature.

Several experiments have been carried out utilizing porous glass beads of a wide range of porosity under experimental conditions equivalent to those utilized in studying the mobile-phase effects with non-porous glass beads. Typical HETP-vs-Reynolds number data encountered are shown in Figure 1. Subtracting out the mobile-phase effects for the data obtained in the porous glass columns leaves the effect of the permeation process upon the observed dispersion. When these data are subjected to a least squares analysis the results show that the observed dispersion due to the permeation process is a linear function of Reynolds number (flow rate). Therefore, the permeation process appears to be controlled by a linear permeation isotherm such that the concentration in the stationary phase (within the pore) is directly proportional to the concentration in the mobile phase. We, therefore, feel that the permeation process is

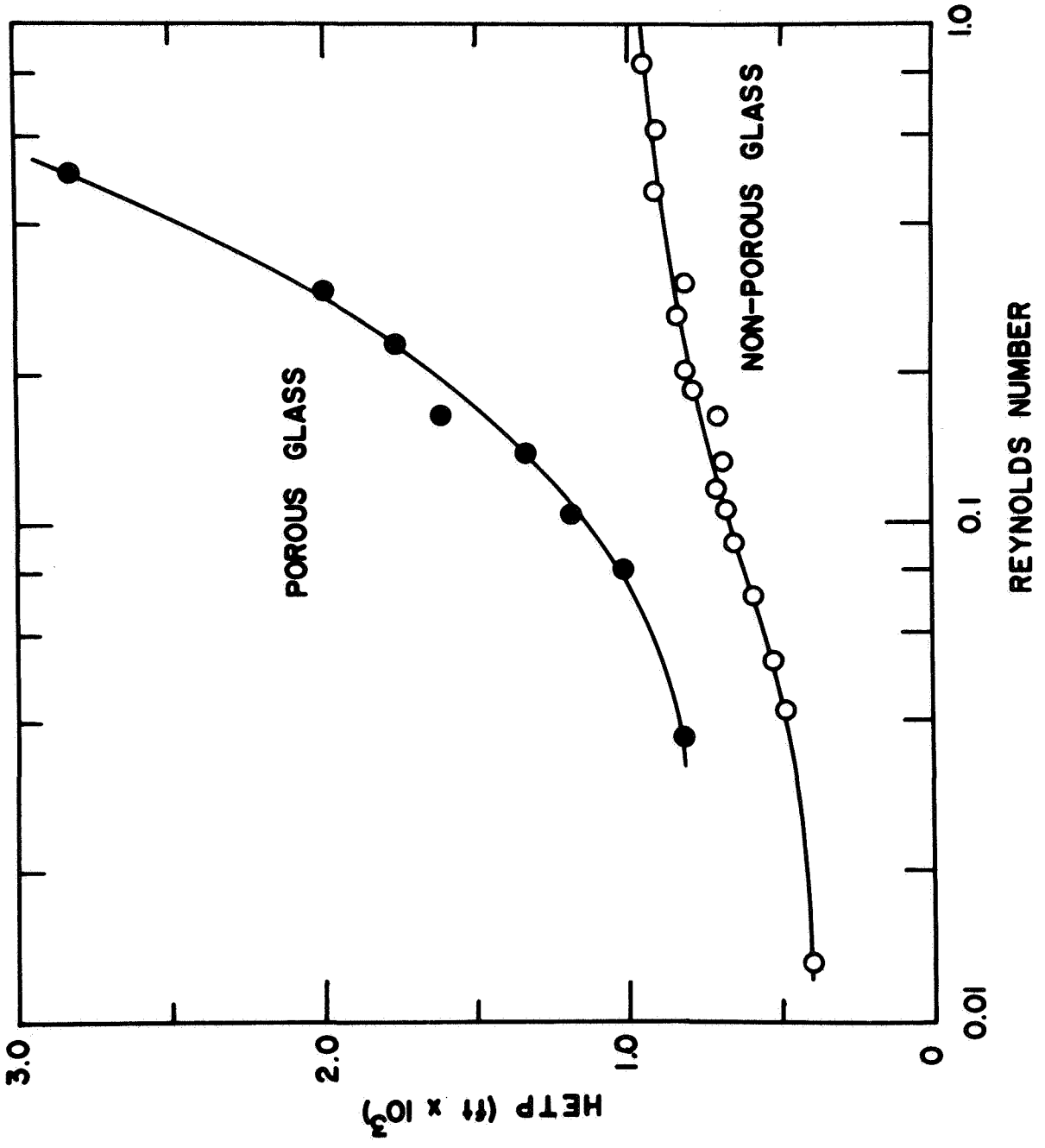
3.0
2.0
1.0
0
HETP (ft x 10³)
0.01
0.1
1.0
REYNOLDS NUMBER
POROUS GLASS
NON-POROUS GLASS

FIGURE 1

diffusion controlled provided other experimental interferences such as adsorption and viscous fingering (concentration) effects are minimized.

The HETP data for the porous glass column (Figure 1) seem to differ greatly from HETP data obtained with the more commonly used crosslinked polystyrene column packing material. These data more closely resemble the curves obtained for mobile-phase effects only. To explain these differences, it is necessary to examine both mercury porosimetry data in the literature and electron photomicrographs of the gel packing materials. Mercury intrusion data show very sharp slopes for the porous glass packings and, in contrast, relatively low slopes for the polystyrenes. These data suggest not only that there are differences in the breadth of the pore-size distribution between the glass and the polystyrene, but also that there may be great structural differences as well. Electron photomicrographs, done outside this laboratory, do indeed show very great differences in the gel structures. Basically, the deep internal pore structure of the glass bead is much more accessible from the pores near the surface of the bead than in the polystyrene beads. Therefore, once a molecule enters a pore in the glass packing material it has more freedom to continue diffusing toward the center of the particle in contrast to the situation in the polystyrene packings. Such diffusion greatly increases the observed dispersion over that due only to mobile-phase effects. We feel that at normal GPC flow rates, because of such differences in pore structure, dispersion in porous glass bead columns is primarily controlled by permeation (mass transfer) effects, while in polystyrene-packed columns dispersion is primarily controlled by mobile-phase effects occurring outside the gel. These results will be submitted

for publication in the near future. Further studies are planned on the concept of eddy diffusion as applied to very low diffusivity solute molecules such as encountered in high polymers. This work has been supported by the Dow Chemical Company, Texas Division, Waters Associates, Inc., Framingham, Massachusetts, and Hercules, Incorporated, Wilmington, Delaware.

CALIBRATION OF GEL PERMEATION CHROMATOGRAPHS

Senior Investigator: F. W. Billmeyer, Jr.

The requirement of high absolute accuracy in the characterization of standard polymer samples for testing calibration procedures for GPC has necessitated a rigorous calibration of our wide-angle light-scattering photometer. This has been completed with good agreement among results obtained with a number of different techniques and reference materials. Eight poly(methyl methacrylate) samples with medium-breadth molecular-weight distribution and three fractions of the same polymer with narrow distributions have been characterized for weight-average molecular weight by light scattering. We have also applied the proper reflection corrections and experimentally-determined refraction corrections to these data to obtain the most accurate results for weight-average molecular weights. These samples have also been characterized for number-average molecular weight by membrane osmometry.

These samples are now being used to test a calibration procedure for gel permeation chromatography using samples with broad molecular-weight distribution. We originally proposed such a procedure in 1966 but have delayed preparation of a paper while the above mentioned series of well-characterized samples was prepared. Early publication of the previously

cited GPC calibration procedure is now anticipated, as well as our work on experimentally-determined refraction corrections in light scattering.

THERMODYNAMICS OF SYSTEMS OF SEMI-CRYSTALLINE POLYMERS AND SOLVENTS

Senior Investigator: F. W. Billmeyer, Jr.

Studies are now complete upon the sorption behavior of toluene vapor in polystyrene at 30°C, using a well-characterized sample with number-average molecular weight of 160,000. Agreement is excellent with data collected by Maron on earlier work with this system. This verifies the accuracy of the transducer response to small pressure changes. Recalibration of the transducer after completion of the sorption run demonstrates that the output is stable with time.

Work will now begin upon the poly(α-olefin) systems, again using toluene as solvent in the range of 30 - 50°C. The first sample to be studied, polybutene-1, is of interest since it exists in at least four polymorphic forms, two of which are stable at room temperature and accessible to our experiments. All forms have been well established by DTA, x-ray, and dilatometric techniques.[1]

Form II of polybutene-1 is a metastable polymorph obtained by crystallizing from the melt. Upon standing at room temperature and atmospheric pressure, it undergoes a spontaneous crystal-crystal transformation to the stable form I. Form III, on the other hand, is obtained by freeze-drying of 10 - 20 per cent solutions or by casting films of the same. Once obtained, form III is quite stable at room temperature and up to about 70°C.

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[1] C. Geacintor, R. B. Miles, and H. J. L. Schuurmans, J. Poly. Sci., 14, 283, (1966) J. Poly. Sci., A-1, 4, 431, (1966).

Polybutene-1 is, therefore, a good choice to emphasize the advantages of the sorption technique for determining solvent activity in the presence of polymer at high concentrations. It has been shown by x-ray analysis and specific volume calculations that form I of polybutene-1 can have crystallinities in the range of 70 - 80 per cent. This should give rise to large differences between the activity calculated by means of the Maron theory from the polymer's dilute solution behavior (osmometry and viscosity) and the activity experimentally observed at high polymer concentrations during the sorption runs. From these activity differences, the actual crystallinity or degree of order of the sample may be determined and compared for verification with the values previously cited.

Because of the inter-relationship of forms I and III, it will be convenient to compare the two. Form I will be run to completion, at which time it is essentially a polymer in dilute solution. Evacuation of all solvent should then yield form III directly.

By careful treatment of the sample, one can obtain a mixture of both I and III. This can be used to illustrate an additional advantage of the sorption technique. A plot of fraction crystallinity (Maron's) versus concentration gives rise to plateau regions corresponding to stable forms of the polymer. Thus, a polymer exhibiting a crystallinity of 80 per cent initially does not retain this value throughout the concentration range. Successive additions of solvent are progressively able to break down the ordered regions and dissolve them, so that relative crystallinity decreases with increasing solvent concentration. But, as the plateau region due to one form decreases and finally disappears, a second crystalline form may then appear which is stable over a different

concentration range. This type of behavior is expected for polybutene-1 and will be investigated from this point of view. The dilute solution measurements will also be performed.

Polyoctadecene-1 polymerized using Ziegler catalysts,[2] resulting in a highly stereoregular structure, is also to be studied. Turner Jones[3] has identified two crystal modifications, I and II, for this polymer. Density calculations give crystallinities of 50 - 70 per cent for the two forms, form II usually having the higher crystallinity.

An attempt will be made to analyze separately the tactic and atactic forms of polyoctadecene-1. This is possible by a technique of hexane extractions developed by Aubrey and Barnatt,[4] in which a sample polymerized by them was found to be about 50 per cent insoluble in the hexane. By analogy with lower polyolefins, the authors assumed that the hexane-soluble and hexane-insoluble polymers are the atactic and tactic forms, respectively.

The separation according to tacticity will be performed followed by sorption runs upon the fractions. Here again, varying thermal histories can be used to obtain mixtures of the two forms, with the result that plateau regions can be seen as with polybutene-1.

This work was supported in part by the Esso Educational Foundation.

STRUCTURAL CHARACTERIZATION OF LINEAR ALIPHATIC POLYESTERS

Senior Investigator: F. W. Billmeyer, Jr.

Analysis of Debye-Scherrer x-ray powder photographs of carefully

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[2] D. W. Aubrey and A. Barnatt, J. Poly. Sci., A-1, 4, 1709, (1966).

[3] A. Turner Jones, Makromol. Chem., 71, 1, (1964).

[4] D. W. Aubrey and A. Barnatt, J. Poly. Sci., A-2, 6, 241, (1968).

crystallized and annealed samples of poly(ethylene adipate), poly(ethylene suberate), and poly(ethylene sebacate) has been completed and the following unit cell dimensions and densities have been calculated:

| | Axis Lengths a | b | c | Cell Angle, β (radians) | Density, g/cm$^3$ |
|---|---|---|---|---|---|
| adipate | 5.47 | 7.23 | 11.55 | 1.98 | 1.364 |
| suberate | 5.50 | 7.25 | 14.10 | 2.00 | 1.300 |
| sebacate | 5.52 | 7.30 | 16.65 | 2.01 | 1.244 |

It is significant that the c-dimensions for each of the polyesters appear to be 0.15 to 0.20 Å shorter than those obtained from similar measurements on oriented fibers. The difference is tentatively attributed to the presence of a twist in the glycol residue which may be partially straightened when orientation is achieved by drawing.

A second, more careful dilatometer study employing the polyester samples of highest density and utilizing very slow heating rates (1$^o$/day or less) has been carried out in order to determine the maximum, and presumably equilibrium, melting points of the three polymers. Specific volume-temperature relationships above the melting point were also measured and extrapolated to give the amorphous density for each polymer at 23$^o$C. In addition, least-squares analysis of the same dilatometer curves have been used to evaluate numerically the specific volume-temperature relationships for the 100 per cent crystalline and amorphous polymers. The results appear below:

| | Equilibrium Melting Point, $^o$C | Amorphous Density (23$^o$C), 9/cm$^3$ | Specific Volume Expansion Coefficient, cm$^3$/g$^o$C: Amorphous | Crystalline |
|---|---|---|---|---|
| adipate | 65 | 1.221 | $.66 \times 10^{-3}$ | $.64 \times 10^{-3}$ |
| suberate | 75.5 | 1.144 | $.70 \times 10^{-3}$ | $.57 \times 10^{-3}$ |
| sebacate | 82 | 1.083 | $.75 \times 10^{-3}$ | $.53 \times 10^{-3}$ |

Examination of optical and electron micrographs of bulk crystallized material prepared in the same way as that for the x-ray and dilatometer experiments has been completed. Optical micrographs show positive (+) spherulites characterized by very grainy appearance and lack of concentric ring pattern. Electron micrographs of fracture surfaces of the same material reveal highly lamellar surfaces with lamellae 80 to 150 Å thick displaying numerous but irregular twists. the irregularity of the twisting presumably explains the absence of interference rings in the optical micrographs and the presence of the thinned lamellae may be the cause of premelting observed in the dilatometer experiment described above.

Heats of fusion of the three polyesters have been measured by differential scanning calorimetry and have been extrapolated to those for the 100 per cent crystalline materials. Entropies of fusion have been calculated using the newly determined melting points. Calculation of the relative contributions of the volume expansion and configurational entropies for the three polymers await completion of compressibility measurements.

At present, attention is focused on the evaluation of the newly determined heats and entropies of fusion in terms of molecular interactions and chain stiffness.

This work was supported by the National Science Foundation.

## POLYMER-SOLVENT INTERACTIONS

Senior Investigator: S. S. Sternstein

The constant volume polymer-solvent interaction cell described

in previous reports is being modified to permit studies which involve the use of liquids at various pressures. The present design is limited to the use of liquids under a nominal gage pressure of one-half atmosphere. It is planned to continue the study of diffusion phenomena, and the new liquid feed system will improve considerably the accuracy of the liquid absorption data. In addition to natural rubber samples, additional experiments on multiphase polymeric composites are planned. Dr. Ramdas Dujari has completed his studies on this project and Mr. William Warner is continuing the study.

## LOW TEMPERATURE THERMODYNAMIC STUDIES

Senior Investigator: G. L. Salinger

Measurements of the thermal conductivity of amorphous polymers have temporarily been halted in order to investigate the specific heat of a variety of polymers. The specific heat measurements indicate that in addition to the acoustic Debye spectrum there exist independent oscillators at low frequencies. These contribute an additional scattering mechanism in the thermal conductivity and must be studied to understand the thermal conductivity.

The specific heat data for poly(methyl methacrylate) (PMMA) and polystyrene (PS) have been reanalyzed since the velocity of sound data at liquid helium temperatures indicated that the Debye specific heat was less than heretofore thought. The excess specific heat is fit with two Einstein modes with characteristic temperatures of 16 and 6.3K for PMMA and 14.5 and 5.5K for PS. The higher temperature modes are consistent with the oscillation of pendant groups near voids. If a libration of the

pendant group in a hindering potential is assumed, the barrier height is near 300 calories/mole (0.014eV) using standard bond lengths and angles to calculate the moment of inertia about the libration axis. Although low, this is not unreasonable in view of the complicated geometry of the monomer units.

The specific heat of a number of polymers with similar pendant groups is being measured in order to correlate the excess specific heat with molecular motions. Results on poly(vinyl acetate), polybutene, and polyethylene are being analyzed. A computer program is being developed to aid in the analysis.

These measurements are being correlated with internal friction, ultrasonic attenuation and spin-lattice relaxation time measurements in cooperation with Drs. Casabella and MacCrone.

DIFFUSION FACILITY

Senior Investigator: H. M. Gilder

We are presently making aluminum-zinc alloys in concentrations from zero to about 20 atomic percent zinc. We are now engaged in solving the rather difficult problem of electrodepositing radioactive $Al^{26}$ onto the alloy specimens from a nonaqueous plating bath. Preliminary indications are that we are obtaining small yeilds of $Al^{26}$ which we are prepared to count in a coincidence arrangement to minimize background. We will then diffuse $Al^{26}$ and $Zn^{65}$ in the alloys, and obtain information on the diffusion coefficients by a radiotracer-lathe sectioning technique. In view of recent work by Heumann and Böhmer on impurity and self-diffusion in aluminum-silver alloys, in which the impurity has a relative valence of -2, it will be important to explore the effect of an impurity with a

relative valence of -1 on the aluminum self-diffusion coefficient.

POLYMERIZATION KINETICS OF METHYL METHACRYLATE

Senior Investigator: F. W. Billmeyer, Jr.

A study of the kinetics of free-radical polymerization of methyl methacrylate at both low and high conversions was completed with the determination of polymerization rates and activation energies and the characterization of the product polymers for molecular weight and molecular-weight distribution by gel permeation chromatography.

A comparison of the overall activation energies for photo-initiated polymerization (corresponding to the combination of rate constants $k_p^2/k_t$) substantiated the fact that the polymerization is diffusion controlled in and beyond the auto acceleration region. The practical result of this is somewhat unexpected: to reach very high conversions most rapidly, it is necessary to polymerize at low temperatures, where the rate at low conversions is low. This has the effect of prolonging the auto acceleration region, in which polymerization is very rapid, to quite high conversions. Complete polymerization is thus reached sooner than it would be if the reaction were started at a higher rate.

The GPC results demonstrated clearly the tremendous broadening of the molecular-weight distribution and increase in weight-average molecular weight first postulated in the senior investigator's 1953 work.

This project has been completed, and the M.Sc. degree has been granted to Mr. Pulley. A paper is in preparation. The work was sponsored by the General Motors Institute.

# SOLID STATE REACTIONS AND PHASE TRANSFORMATIONS

# SOLID STATE REACTIONS AND PHASE TRANSFORMATIONS

A primary goal in the study of solid materials is the predictable attainment of specific structures together with the concomitant ability to alter the structure of solids through the use of solid state reactions and phase transformations. On this basis, the foundation of solids research, the coupling of structure to property relationships becomes a definitive reality. The research reported in this section is directed towards this goal, the achievement of basic understandings as to the nature of a variety of solid state reactions and phase transformations for a broad grouping of solid materials, with specific interrelationships to the overall view of materials research outlined in the other report areas. While the activities in this program area are given in detail following this introductory section, the highlights of the research results during the past program period are as follows:

Several studies have been directed towards achieving an understanding of the factors controlling the kinetics of solid state phase transformations. Two areas, which have significant practical application, are precipitation from solid solution and the martensite transformation in steels. Both of these phase transformations are not clearly understood, yet are utilized as the basis for producing the majority of high-strength alloys. During this program period, the kinetics of cellular precipitation in nickel base alloys appears to be defined, the solubility of interstitial elements predicted for the group VIa elements, while quench rate studies have provided data which links the kinetics of the martensite transformation to the mechanical properties of the initial phase. In studies of the effects of ionizing radiation on the ferroelectric behavior of Rochelle salt, it has been found that irradiation of the non-ferroelectric phase inhibits the

transformation to the ferroelectric phase. However, irradiation effects are more pronounced for irradiation carried out above the ferroelectric range as compared to lower temperature irradiation. Indeed, for the lower temperature irradiation, the full effects of the damage do not appear at once upon heating the crystal to the ferroelectric range, but rather build up slowly. The specific heat of a series of polymers were systematically studied in the glass transition region in order to determine the effect of thermal history and heating rate. The hole model was used to describe the measured data.

Other programs in this area have centered on vapor-solid phase reactions. High temperature equilibrium vaporization studies have been pursued in order to determine the stability of the condensed phase and the thermodynamic properties. During this period, kinetic studies on MnS and MnSe under free evaporation conditions have been completed. In a reverse sense to these equilibrium vapor-solid phase studies, investigation has continued in the non-equilibrium reversible oxidation of aluminum.

During this period an electron microprobe was obtained for use in a wide range of research activities under this program. The probe, a Materials Analysis Corporation Model 400S, has been installed and a number of research personnel have now been trained in its operation.

## REVERSIBLE OXIDATION OF ALUMINUM

Senior Investigator: G. S. Ansell

Previous work in this laboratory has shown that $Al-Al_2O_3$ SAP alloys heated in the hot stage of an electron microscope formed a reversible type of aluminum oxide that had not been previously reported. In order to determine the nature of this rather unexpected event, a program to study the formation of reversible oxides of high purity aluminum in a more controlled atmosphere has been undertaken. In order to proceed with this study, the hot stage electron microscope has been modified to provide atmospheres of $10^{-7}$ torr ambient at the specimen stage, as compared with $10^{-4}$ to $10^{-5}$ torr normally achieved, together with gas monitoring using a monopole mass spectrometer. In addition, an ultra high vacuum system with $10^{-9}$ torr capability has been modified to permit controlled oxidation of similar aluminum specimens. Studies are now in progress using both systems to study the oxide formation as a function of the nature of the prior amorphous aluminum oxide previously formed on the aluminum specimen surface, the purity of the gaseous environment and the thickness of the aluminum specimen.

## MARTENSITE TRANSFORMATION

Senior Investigator: G. S. Ansell

The kinetics of the martensite transformation in the Fe-C system have proved elusive. As a result of recent work in this laboratory, it is felt that this transformation may be controlled by the shear strength of austenite. For this reason, an investigation of the kinetics of the

martensite transformation as a function of austenite strength has been undertaken.

Several approaches are being used in this study. In the first, the effect of solute elements of varying diffusivity in austenite upon the nature of athermal stabilization during rapid quenching is being studied. We have established that such rapid quenching increases dramatically, as much as 200$^{o}$F, the $M_s$ temperature of 52100 steel. We now wish to establish the role of the solute elements in steel upon this aspect of the transformation kinetics. This program has centered about determining the effect of quench rate upon the $M_s$ temperature of the Fe-C-X alloys in which the nominal $M_s$ temperatures of these alloys are identical and the effect of the X element on carbon diffusivity is quite variable. This program is now in progress. The results to date indicate that the quench rate effect of the $M_s$ temperature is directly related to the rate of carbon diffusivity in the austenite as predicted by the strengthening model previously proposed.

The second approach has been to relate the entire transformation kinetics to the flow stress characteristics of the austenite. In order to accomplish this, a series of oxide dispersion-strengthened Fe-C-Mn alloys have been prepared in which the oxide content of the alloy series is varied from 0 to 15 volume per cent in order to vary the shear characteristics, but not the free energy of the alloys. These alloys were prepared by powder metallurgy techniques. Preliminary study shows that the temperature for the start of the transformation decreases with increasing oxide content, as would be predicted by the theoretical arguments. These programs are currently in progress.

PRECIPITATION KINETICS

Senior Investigator: G. S. Ansell

The studies of the formation of precipitate phases from solid solutions have followed two avenues of interest. In the first, the growth kinetics of cellular precipitation has been studied in detail using both conventional and hot stage electron microscopy in a series of Ni-Co-Al alloys over a wide range of cobalt contents. In this study, interest has centered on the details of the growth process, particularly the relationship between the precipitate phase and the moving boundary. It appears quite clear that the precipitate phase leads the moving boundary with the growth kinetics controlled by the boundary mobility. This research area is now completed.

The second area of study has centered upon the solubility of interstitial elements in transition metal alloys, particularly of the group VIa element series. A theoretical analysis of the solubility of the interstitial elements in these alloys was made. It was found that the change of system free energy as the interstitials are formed from the atomic state during the dissolving process is dominated by the electronic interaction. This electronic interaction energy is characterized by the energy band structure, a rigid band model being used for the case of these bcc alloys. The minimum exhibited in the density-of-states curve, caused by the overlapping of subbands, gives rise to an unusual free energy change. Numerical calculations predict the interstitial solubilities in good agreement with experimental results.

ELECTRON MICROPROBE FACILITY

Senior Investigator: G. Judd

The research funding of the electron microprobe facility was initiated during the past half year and was used to assist in the outfitting of the microprobe laboratory. The electron microprobe was acquired in July, 1968, and the period of September 1, 1968 - February 28, 1969, has been spent primarily in the training of personnel to operate the instrument and to perform research projects using the instrumentation method.

The introductory phase is completed and there are six faculty and students who have, to varying degrees, been trained on this instrumentation. These researchers are from several different groups: Electron Microprobe, Defect Structures, Powder Metallurgy, Friction and Wear, and Geology. Interest in the adoption of the microanalysis technique has also been displayed by the Welding, Melting and Solidification, Fiber Composite, Corrosion and Dental Materials groups, and it is anticipated that the number of individuals and research groups using this instrumentation will increase markedly in the next year.

The application of this facility in the various research projects to date has varied from a qualitative identification of elements present to quantitative step scan analysis of chemical compositions. In particular. in the investigation of precipitate free zones at grain boundaries, where the mechanical and corrosion properties of alloys exhibiting the zone structure can be correlated with microstructure, the microprobe is being used to study the concentration profile in a series of alloys to determine

the mechanism causing the precipitate free zones. Further, since composition is an important variable in any precipitation process, a precise understanding of the composition profiles in the alloys should yield valuable information for alloy development.

In addition to the grain boundary segregation studies, work on the chemical composition of various geological samples, the identification of wear particles, and the composition gradients in internally oxidized silver alloy has been started by other research groups.

## DIFFERENTIAL THERMAL ANALYSIS OF THE GLASS TRANSITION REGION

Senior Investigator: B. Wunderlich

Differential Thermal Analysis was used for a systematic study of the effect of thermal history and heating rate on the specific heat of glasses in the glass transition region. The materials studied were poly(methyl methacrylate), polystyrene, poly(vinyl chloride) and polymeric selenium. Cooling rates were varied by more than five orders of magnitude. On heating and cooling the specific heat jump at $T_g$ occurred at higher temperatures for faster rates of temperature change. On heating a glass formed by slow cooling from the liquid state, a large peak was superimposed on the rise in specific heat at $T_g$. The peak temperatures could be expressed by $T_p = A + B \log q$, where q is the heating rate and A depends on thermal history, being lower for higher rates of cooling. The hole model is used for the description of the measured specific heats. Below $T_g$ the hole equilibrium is assumed to be frozen, but in the liquid state hole equilibrium is reached practically instantaneously. In the transition region the approach to equilibrium is governed by one relaxation only. This relaxation time

can be determined from the energy and volume of holes and DTA data on $T_p$, q and the specific heat at $T_g$.

NUCLEAR MAGNETIC RESONANCE FOR SOLID STATE REACTIONS AND PHASE TRANSFORMATIONS

Senior Investigator: P. A. Casabella

The study of the effects of ionizing radiation on the ferroelectric properties of Rochelle salt have been continued. This work uses the $Na^{23}$ nuclear magnetic resonance as a probe to study the behavior of the crystal after it has been exposed to $Co^{60}$ $\gamma$ rays. The most recent studies have been concerned with the effects of irradiation outside the ferroelectric temperature range, which is only from $-18^{o}C$ to $+24^{o}C$. Irradiation has been carried out both above and below the ferroelectric range, and then the crystal was studied in the ferroelectric range.

In both cases the spontaneous polarization in the ferroelectric range was reduced by the irradiation, and the temperature range over which the crystal was ferroelectric was reduced. However, for the same radiation dose effects were far more pronounced for the higher temperature irradiation than for the lower. This implies that more of the damage centers responsible for these effects are created at the higher temperature than at the lower. In addition, when the crystal irradiated at the lower temperature is first brought into the ferroelectric temperature range, the full effects of the radiation damage do not appear at once, but slowly build up over a period of a few hours. This is interpreted to mean that at low temperatures the $\gamma$ rays create defects that are not effective in reducing the spontaneous polarization, but when the temperature is raised these defects convert to some other form, and this form is effective. This

two stage process apparently results in the lower number of defects created by the low temperature irradiation. These studies will be continued in an effort to identify these defects.

## THERMODYNAMIC STUDIES AT HIGH TEMPERATURES

Senior Investigator: H. Wiedemeier

The objectives of this work are the determination of thermodynamic and kinetic properties of transition metal compounds. Vaporization studies at elevated temperatures represent an excellent tool to determine such properties which are interpreted in terms of stabilities of condensed phases and of gaseous molecules of these materials.

Kinetic studies on MnS and MnSe under free evaporation conditions have been completed. The rate of evaporation from (111) faces of vapor grown single crystals of the above materials was determined as a function of temperature and time. The vaporization coefficient is smaller than unity for both compounds indicating the existence of a rate determining step in the sublimation of these materials. Through the application of transition state theory the experimental data were evaluated in terms of enthalpies and entropies of activation. In accordance with Volmer's concept of stepwise evaporation a mechanism of vaporization is suggested for the manganese chalcogenides. Based on this scheme and on thermochemical and structural considerations for the individual steps involved the rate determining step is most likely the bond breaking process in the very beginning of the vaporization sequence. These results are in agreement with the behavior of other transition metal chalcogenides.

Recent publications indicate that the mode of vaporization of II-VI compounds under equilibrium conditions is still somewhat uncertain. The question of congruency is of decisive importance for the evaluation of vapor pressure measurements and of practical significance for possible changes of solid state properties of these materials when used at higher temperatures. Studies are underway to solve this problem by vaporization experiments employing vacuum microbalance techniques. The material under investigation is of extremely high purity through repeated gas phase transport reactions. The vaporization studies are carried out in various temperature ranges. In each case the sublimation products are recovered on condensation shields and are characterized by X-ray diffraction and chemical analysis techniques. The same procedure is applied to the condensed phase residue. Through this combined experimental approach it will be possible to clarify the mode of equilibrium sublimation of these materials.

# MECHANICAL PROPERTIES AND STRENGTHENING MECHANISMS

# MECHANICAL PROPERTIES AND STRENGTHENING MECHANISMS

Research in this area includes studies on dispersion-strengthened alloys, hardness of glass, rheology of liquid polymers, mechanical behavior of amorphous and crystalline polymers, and properties of composites. Some highlights of results obtained during the past six months include the following:

Yielding tests in tension and compression demonstrated that yielding in two-phase alloys is sensitive to both normal stress and shear stress. Previous theories of dispersion strengthening have considered only shear stress.

A torsion pendulum apparatus is being used to measure activation energies for grain boundary sliding in two-phase alloys. These data should aid in assessing the role of grain boundary sliding in superplasticity.

Plastic yielding studies on glassy polymers in biaxial stress fields have established that "crazing" is a localized yielding in response to the normal stress.

Structure-properties studies on crystalline polymers suggest that long-range elastic behavior may be a response of small deformed crystals rather than an oriented, amorphous phase.

Characterization of crystal plane orientation in graphite fibers at the surface and at the interior of the fiber have been related to shear strength in graphite fiber composites.

GALLIUM OXIDE - SILVER ALLOYS

Senior Investigator: F. V. Lenel

Gallium oxide - silver alloys are being produced by two methods:

Decomposition of sprayed and freeze-dried silver nitrate-gallium nitrate mixtures and subsequent consolidation of the alloy.

Internal oxidation of silver-gallium alloys. Emphasis is being put on the study of the kinetics of internal oxidation of silver-gallium alloys. When strip of an alloy of a given composition is oxidized at a constant oxygen pressure, the size and spacing of the oxide particles is small at the surface and increases with increasing distance from the surface. When the oxygen pressure is increased during the internal oxidation treatment dispersions with uniform particle size and spacing are being produced. At the present time the morphology of the oxide dispersion in strip samples, 0.040" thick with 0.2 and 1.0 atomic percent gallium internally oxidized in air at 900$^{o}$C is being studied. On the basis of the results of this study the necessary information for producing 0.010" thick strip with uniform size and spacing of oxide particles is being developed.

ALUMINUM

Senior Investigator: F. V. Lenel

Samples of atomized aluminum alloy powders with 0.6, 1.2 and 1.8 weight per cent copper and with 0.5, 1, 2 and 4 weight per cent magnesium received from Illinois Institute of Technology Research Center are being processed into samples for creep testing using the following procedure:

1. Remove the +20 micron size fraction by microsieving

2. Cold press the -20 micron fraction at 20,000 psi into ½" diameter compacts

3. Vacuum dehydrate the compacts at 540°C for at least 10 hours

4. Hot press the compacts at 540°C at 80,000 psi for 20 minutes

5. Extrude the hot-pressed compacts into 1/8" diameter wire at 540°C

6. Roll the extruded wire into 0.020 - 0.025" thick strip

7. Recrystallize the strip at 580°C and cut into specimens with a 1/4" x 5/8" gauge section

An apparatus for creep testing the samples has been built. A technique for characterizing the microstructure of the material by replication and by transmission electron microscopy has been built.

DISPERSION STRENGTHENING MECHANISMS

Senior Investigator: G. S. Ansell

One aspect of the role of a second phase in dispersion-strengthening that has received little attention has been the necessity of strain compatibility at the two-phase interface in order to retain structural integrity. This effect has particular import as concerned not only with the initiation of voids and microcracks which can lead to fracture but also to the reduction in gross flow strength response. During the past program period the yielding behavior, in both tensile and compressive modes, has been studied for two dispersion-strengthened alloys, TD nickel and an AL - $Al_2O_3$ SAP-Type alloy. The results of this study have demonstrated that the yielding behavior of two-phase alloys is sensitive to the level of normal stress as well as the level shear stress. This is particularly important since up until this time, all theories of dispersion

strengthening have been based only on shear stress dependent models. Work is now underway to couple these results with studies of localized plastic deformation and void formation during plastic strain by means of transmission electron microscopy.

HARDNESS OF GLASS

Senior Investigator: J. D. Mackenzie

The hardness of glass is usually measured by some form of indentation or scratching method. It has been found that the manner in which a scratch or indentation is formed on glass is very different from that on a crystalline solid. Two new mechanisms leading to formation of indentations on glass are now evident. How glass structure and bonding can affect hardness are now being studied. The flow during and after indentation of $SiO_2$ and alkali-oxide-$SiO_2$ glasses is being studied.

SUPERPLASTICITY

Senior Investigator: Laurence Jackman

Internal friction studies are being performed on Al-Zn alloys with compositions in the range of the eutectoid in order to learn more about the mechanism responsible for the superplastic behavior exhibited by some metallic materials. The internal friction peak of most interest is that due to grain boundary sliding, since grain boundary sliding is one of the more strongly supported mechanisms proposed to explain superplasticity.

The grain boundary peak has been observed using an inverted torsion pendulum apparatus in the frequency range of 1 cps. Techniques

are now being developed to accurately determine the activation energy associated with grain boundary sliding from these peaks. These activation energies will be compared to activation energies obtained for the deformation of these alloys while exhibiting superplasticity. The effects of amplitude and frequency associated with damping due to grain boundary sliding are also being examined, and the structure of the grain boundary peak is being analyzed very carefully because of the possibility that the peak actually consists of two or three superimposed peaks. This is a possibility because three types of grain boundaries are present in these two-phase alloys. The influence of grain size, composition, and heat treatment on the grain boundary peak will also be examined.

PLASTIC YIELDING STUDIES

Senior Investigator: S. S. Sternstein

Studies of the formation of crazes in biaxial stress fields have established the stress field criterion for this form of yielding in glassy polymers. The results on PMMA are shown in Figure 2 for three different temperatures. It has been shown that the criterion for crazing is not attributable to shear yielding. Thus, there are two distinct forms of yielding in glassy polymers, namely, shear yielding and normal stress yielding (crazing). The results of Figure 2 suggest a simple model in which the normal stress yielding is considered to be the result of two factors. Firstly, the isotropic component of the stress tensor determines the level of molecular mobility, for a given temperature. Secondly, a stress bias is required to achieve the uniaxial orientation and yielding which results in the formation of a craze. This model suggests that the

stress bias should be a linear function of the reciprocal of the first stress invariant. The reciprocal is used because an increase in mobility due to a dilatational stress should result in a lower stress bias required for yielding. The results of Figure 2 are replotted in Figure 3 and show that this is indeed the case.

The more conventional shear yielding of PMMA has also been studied in biaxial stress field. The results are shown in Figure 4 where the octahedral shear stress is shown to be a linearly decreasing function of the mean normal stress (one-third of the first stress invariant). Figures 3 and 4 have been used as a basis for linear extrapolation and the complete yield envelopes for both shear and normal stress yielding plotted in Figure 5.

Of particular interest is the observation that the two envelopes cross in the second and fourth quadrants of stress space. Physically this corresponds to a level of mean normal stress at which nearly constant volume shear yielding is more easily accomplished than the highly dilatational normal stress yielding. Since the formation of crazes always precedes crack propagation, the crossover point represents a stress field induced, brittle to ductile transition.

## BIAXIAL VISCOELASTIC STUDIES

Senior Investigator: S. S. Sternstein

The results of the Plastic Yielding Studies are being used to develop an understanding of the toughening mechanism in glassy polymers which are modified by the inclusion of a dispersed rubbery phase. In such systems it is believed that the dispersed phase promotes yielding

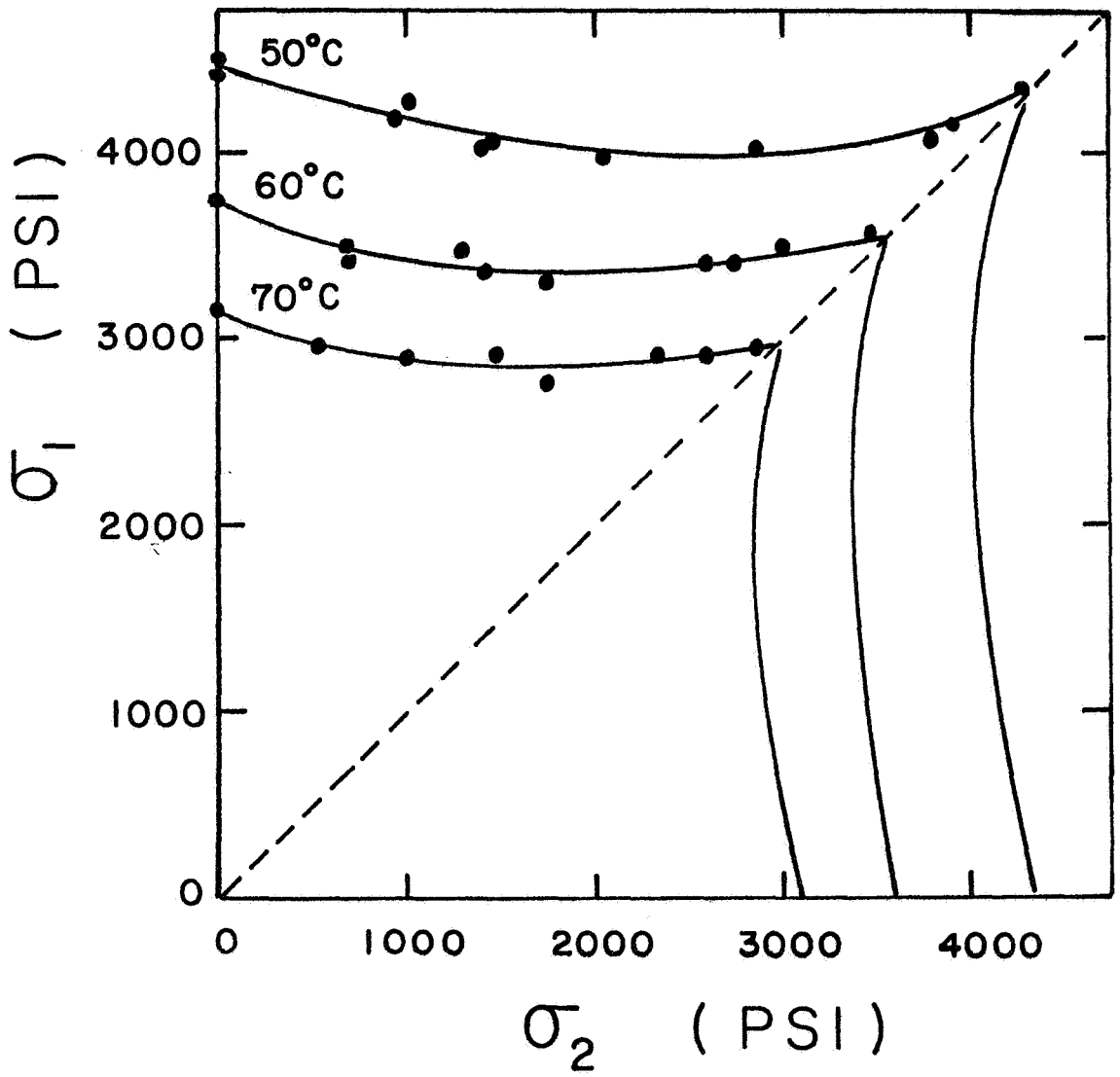

50°C
60°C
70°C
4000
3000
2000
1000
0
$\sigma_1$ (PSI)
0
1000
2000
3000
4000
$\sigma_2$ (PSI)

FIGURE 2

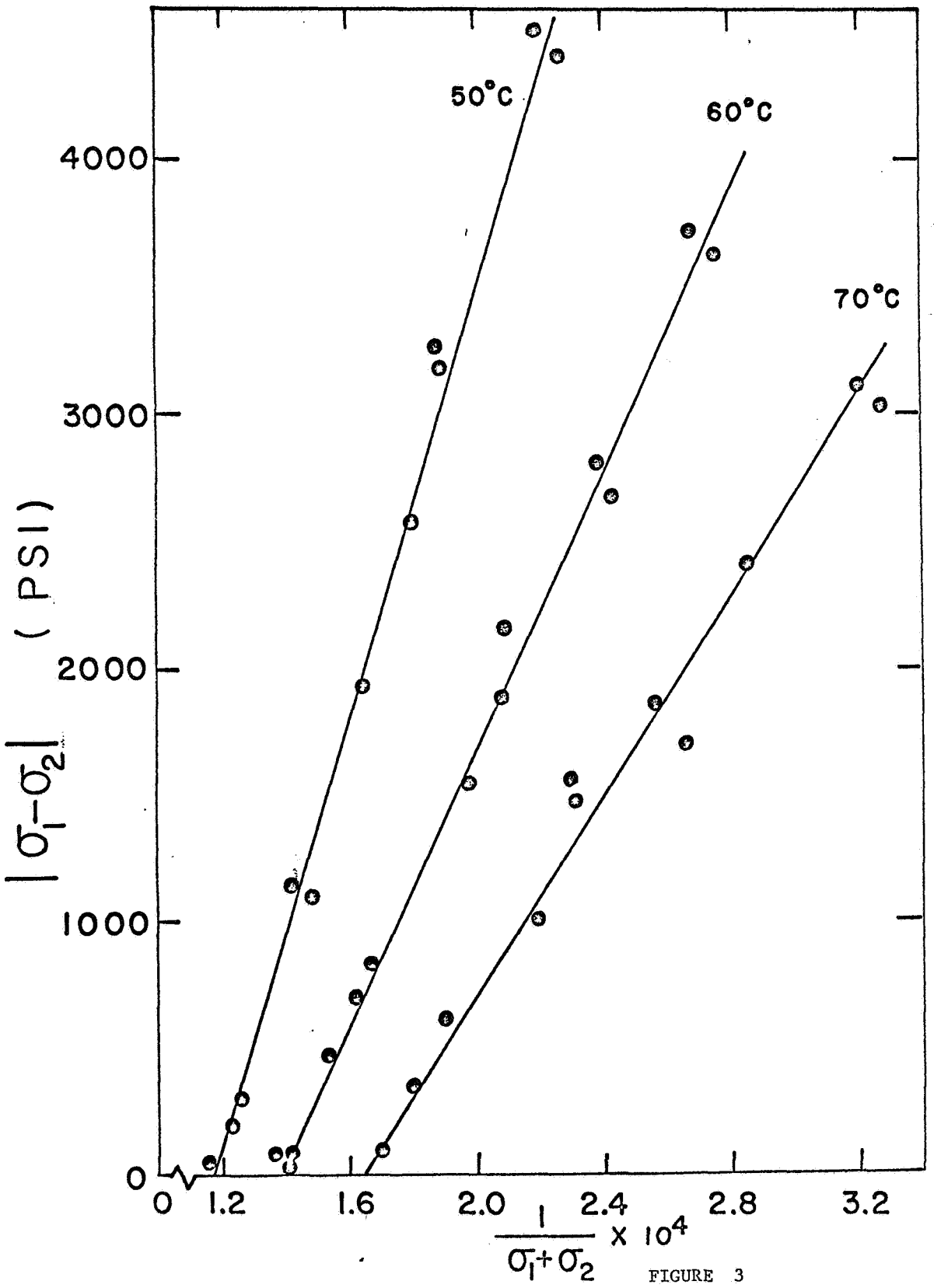

50°C
60°C
70°C
4000
3000
2000
1000
0
$|\sigma_1 - \sigma_2|$ (PSI)
0
1.2
1.6
2.0
2.4
2.8
3.2
$\frac{1}{\sigma_1 + \sigma_2} \times 10^4$

FIGURE 3

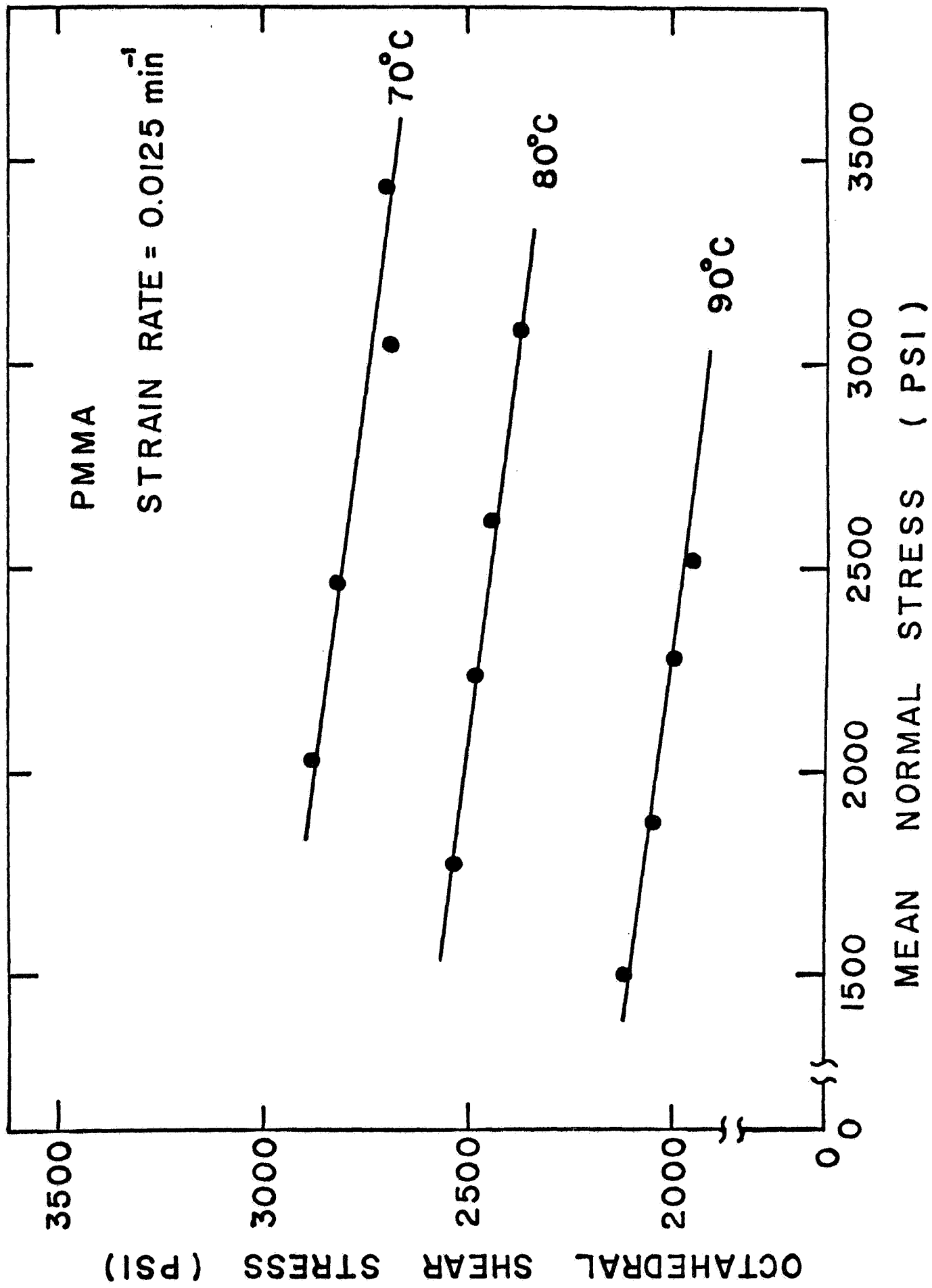

PMMA
STRAIN RATE = 0.0125 min$^{-1}$
70°C
80°C
90°C
3500
3000
2500
2000
0
0
1500
2000
2500
3000
3500
MEAN NORMAL STRESS (PSI)
OCTAHEDRAL SHEAR STRESS (PSI)

FIGURE 4

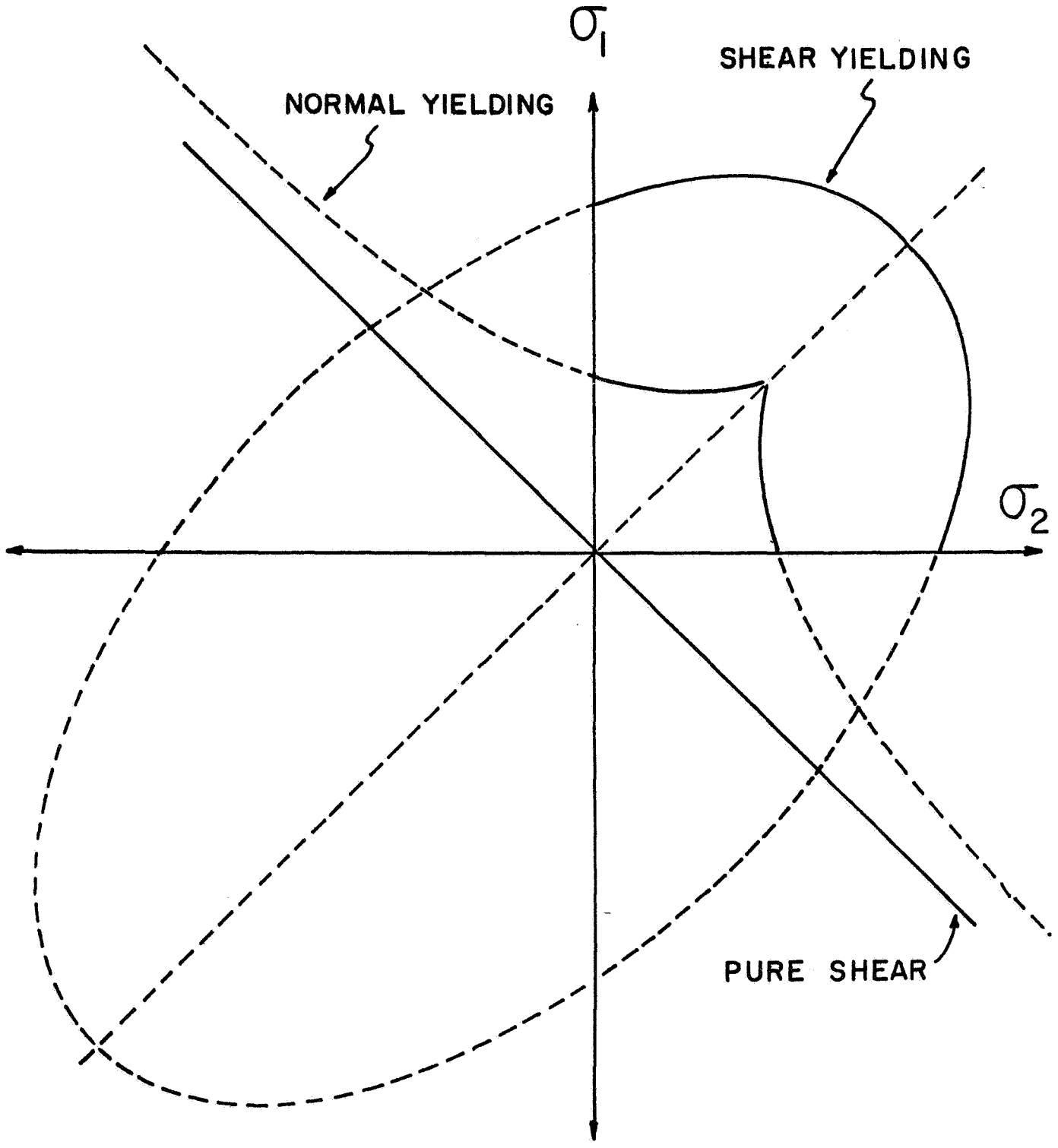



FIGURE 5

phenomena in the glassy matrix by enhancing the stress field conditions required for such yielding. To study the effect of dispersed phases on the viscoelastic properties of the glassy matrix, a biaxial torsion pendulum was developed. Some preliminary results are now available. In Figure 6 is shown the loss factor (tan $\delta$ ) as a function of frequency for various levels of applied axial load to the torsion sample. The sample data are on a styrene-butadiene-styrene emulsion polymerized impact polystyrene. It is noted that the polystyrene $\beta$ peak is shifted to higher frequency (or to lower temperature at constant frequency) by the application of an axial load. Figure 7 shows that the activation energy of this dispersion is lowered by axial loading. Such results can be interpreted in terms of the effect of the stress concentrating dispersed phase on the mobility of the glassy matrix material in the vicinity of the rubbery particles. A mechanism for impact strength enhancement is emerging from such considerations.

## MORPHOLOGY AND COLD DRAWING OF POLYMERS

Senior Investigator: David Hansen

Cold drawing of crystalline polymers alters the morphology in curious and unique ways to yield fibers and films of desirably enhanced properties. In this study these morphological features are being characterized by light microscopy, electron microscopy and x-ray diffraction. From these characterizations we are developing a description of the interaction of large (micron size spherulites) and small (100 Angstrom crystals) entitities in the drawing process. A specific objective is to identify the origins of and conditions for "fibrillation";

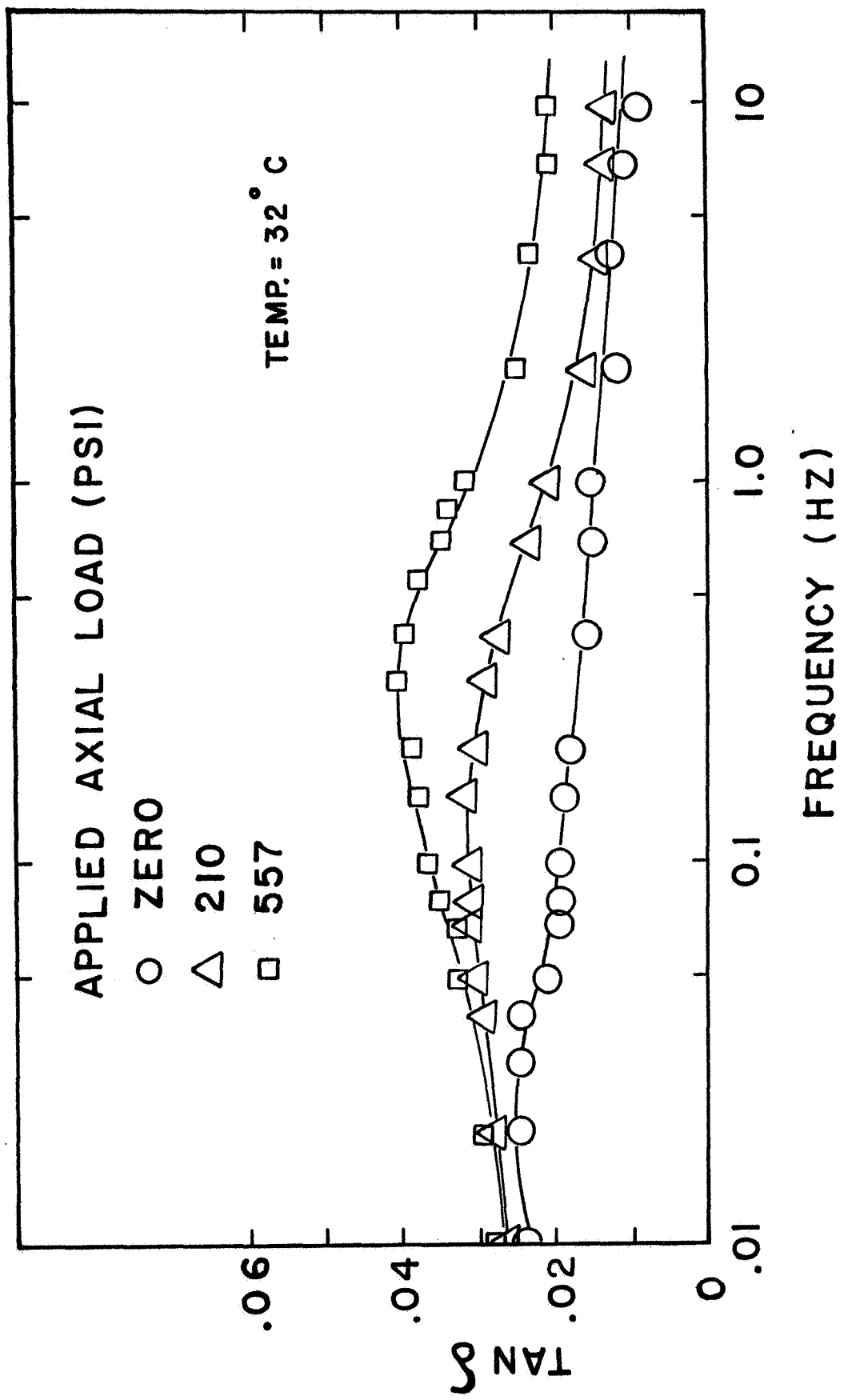

APPLIED AXIAL LOAD (PSI)
ZERO
210
557
TEMP.= 32° C
TAN δ
.06
.04
.02
0
.01
0.1
1.0
10
FREQUENCY (HZ)

FIGURE 6

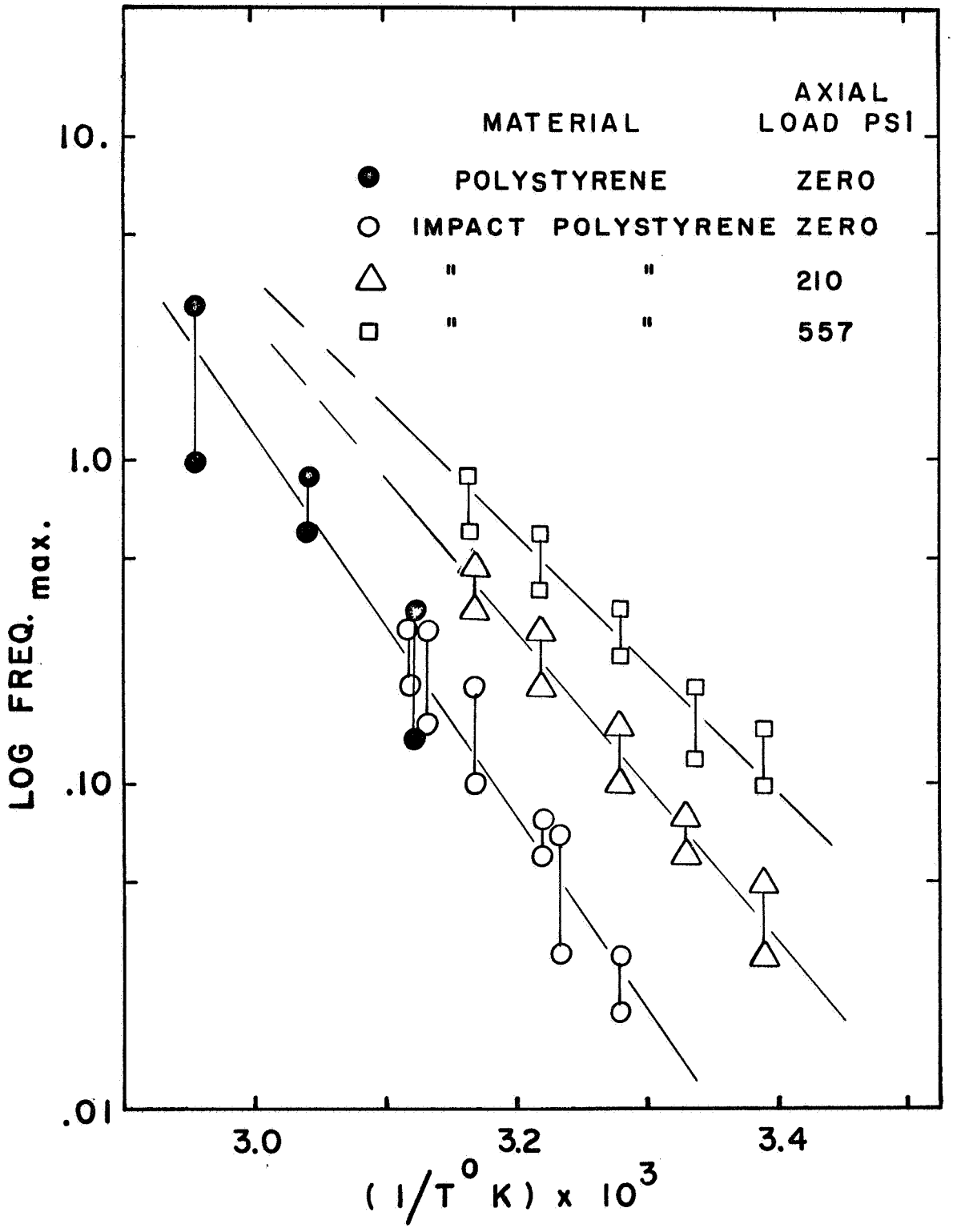

MATERIAL
AXIAL LOAD PSI
POLYSTYRENE ZERO
IMPACT POLYSTYRENE ZERO
" " 210
" " 557
10.
1.0
.10
.01
LOG FREQ. max.
3.0
3.2
3.4
( 1/T° K ) x 10³

FIGURE 7

the development of submicroscopic fibrous structure.

PROPERTIES OF COLD DRAWN CRYSTALLINE POLYMERS

Senior Investigator: David Hansen

The general character of the mechanical behavior of amorphous polymers termed viscoelastic is also characteristic of crystalline polymers. Typically, however, polymers are seldom, if ever, completely crystalline and the properties of a macroscopic sample reflect the composite effect of crystalline and amorphous material. In this study we are seeking to delineate the contribution of the crystalline phase to the macroscopic mechanical response. To this end creep, relaxation and thermomechanical measurements are being made on cold drawn polyethylenes of different crystallinity and containing crystals of different sizes. The mechanical properties tests are being closely coupled with morphological examinations.

The results to date suggest that many aspects of fiber or film behavior commonly attributed to "amorphous regions" may be direct responses of small, deformed crystals.

THE FIBER-MATRIX INTERFACE IN HIGH MODULUS GRAPHITE FIBER COMPOSITES

Senior Investigator: R. J. Diefendorf

High modulus graphite fiber composites offer a higher modulus to weight ratio than with any other fiber and at a potentially low cost. However, a major problem has been the poor interfacial shear strengths between the graphite fiber and the matrix. Although our studies were made to determine the nature of the graphite fiber-epoxy interface, the

structural characterizations of the graphite fibers apply to any system.

The crystallographic nature of the fibers was determined by optical, electronoptical, x-ray and electron diffraction studies. Electrons penetrate the outer skin of the 8 μ fibers to a depth of only 2000Å. Hence, electron diffraction is an accurate way of measuring the orientation of the crystallites near the surface. X-ray diffraction, on the other hand, averages the orientations present throughout the fiber since x-rays pass through the entire fiber. These two methods allow the surface and the interior of the fibers to be observed and analyzed separately. Although both x-ray and electron diffraction show a strong preferred orientation of the basal plane parallel to the fiber axis, electron diffraction generally gives a higher preferred orientation. While this could be anticipated from processing, it does prove that the basal planes are more parallel to the fiber at the surface than in the bulk.

Preferred orientation in the radial direction was determined optically with polarized light, and with dark field electronmicroscopy. Optical observations at 1650x with polarized light on polished cross-sections were used to determine extended areas of preferred orientation. PAN based fibers were symmetrical with a low preferred orientation of c-axis perpendicular to the surface. The preferred orientation of some samples was high near the surface and it appeared that graphitization had occurred at local points on the surface. Rayon based fibers showed lower structure within the fiber. A low degree of preferred orientation was noted followed the crenulated surface. However, a relatively small portion of fibers would show areas with high preferred orientation. These areas appeared to originate at or near the surface, with the

c-axis perpendicular to the surface. In some cases these areas would be large enough to allow an easy shear failure path to split the fiber.

Preliminary polarized light observations on fibers indicated that the optical anisotropy of the outer surface of fibers decreased with increase in modulus. Since electron diffraction had shown that the surface preferred orientation of basal planes parallel to the fiber axis increased with increasing modulus, the decrease in optical anisotropy proved that an increase in preferred orientation of the c-axis perpendicular to the surface is associated with increased modulus. Dark field electron microscopy, using the 002 spot, convincingly showed this to be the case also.

Our studies showed similar preferred orientations of the basal planes parallel to the fiber axis as have earlier studies. In general, the preferred orientation of the basal planes in the axial direction is higher at the outer surface than in the bulk. The preferred orientation of the basal planes in the radial direction is c-axis normal to the surface and increases with modulus. Therefore, as the modulus increases more and more basal plane (low energy) surface is exposed. Unless this surface is etched, poor wetting and bonding can be expected, and poor composite shear strength will result.

# ELECTRONIC AND PHYSICAL PROPERTIES OF MATERIALS

# ELECTRONIC AND PHYSICAL PROPERTIES OF MATERIALS

In this section are reported experiments having as their primary aim to understand an electronic or thermal property of a system per se rather than use the property as a tool toward understanding other aspects of the solid. A large variety of materials are being studied.

One class of materials being studied is polymers. Crystallization during polymerization not only raises the polymerization temperature but changes the physical properties of the polymer. Orientation of a polymer changes its structure and affects its thermal conductivity. Sound velocity measurements are being used to learn about the elastic moduli and also to determine the limiting value of the specific heat at $0^{o}K$. The difference between this value and the calorimetrically determined heat capacity at low temperatures may be related to the analastic relaxation measurements also reported here.

In metals, elastic constants of mercury have been measured and an investigation of the effects of localized magnetic impurities in alloys is being initiated. Dielectric relaxation is being used to understand the conduction mechanism in semiconducting glasses.

## IRREVERSIBLE THERMODYNAMICS OF THE SOLID STATE OF LINEAR HIGH POLYMERS

Senior Investigator: B. Wunderlich

Progress toward the study of crystallization during polymerization was made. The equipment to polymerize paraxylylene has been assembled. The monomer is produced by vacuum pyrolysis at approximately 400°C. The monomer as a diradical condenses to the polymer on a solid surface cooled below 30°C. After nucleation it will be attempted for single crystal growth to raise the polymerization temperature to 350°C, close to the polymer melting temperature. The first set of experiments yielded polymer which is presently being analyzed with respect to its physical properties.

## THERMAL CONDUCTIVITY OF CRYSTALLINE POLYMERS

Senior Investigator: D. Hansen

The basic anisotropy of a high polymer molecule can lead to highly anisotropic macroscopic properties in oriented, crystalline polymers. It is not clear, however, what features of structure determine the limits of practically attainable anisotropy in the thermal conductivity. In this study we are measuring the thermal conductivity of polyethylenes, after controlled crystallization, as a function of orientation. We have not completed enough experimental work for conclusions at this time.

## ANALASTIC RELAXATION

Senior Investigator: R. K. MacCrone

High precision mechanical loss measurements have been made on

the polymer, polymethyl methacrylate, at low temperatures. It has been found that two relaxations occur. It is believed that the structural entities responsible are those which also give rise to excess specific heat; and polymers are thus homologous to glasses, where both these phenomena are observed. More detailed experiments are planned and the theoretical interpretation continues.

SECOND ORDER ELASTIC CONSTANTS

Senior Investigators: H. B. Huntington
G. L. Salinger

The measurements of the elastic constants of anthracene have been finished and submitted for publication.

The measurements of the elastic constants of single crystal mercury have been checked and the data are being analyzed. The constants are only approximate, and due to changes in personnel the measurements will probably not be repeated. However, since this is the first direct measurement of the elastic constants of mercury the data will be published. The last published measurement was the stiffness measurements of Gruneisen and Schell of 1934.

The measurements of the velocities of longitudinally and transversely polarized ultrasonic waves in polymers are being continued. From these measurements, we obtain the Debye contribution to the specific heat of the polymers. These are used in conjunction with calorimetric measurements of the specific heat at low temperatures to determine the excess specific heat (reported on in the Structural Characterization and Synthesis section). From these measurements, the second order Lamé

constants are also obtained. We presently have measurements on polytetrafluorethylene, polyethylene, polybutene, polyvinyl acetate, polystyrene and polymethyl methacrylate at liquid nitrogen temperatures. The temperature dependence of the velocity will be measured in the next six months. This work is sponsored by the National Science Foundation.

THIRD ORDER ELASTIC CONSTANTS

Senior Investigator: H. B. Huntington

The experimental investigation of beam mixing for one of the pure mode cases in NaCl as well as for fused silica is now complete. In both cases it consisted of mixing together a longitudinal wave of 30 MHz with a transverse wave of $y < 30$ MHz to give a transverse beam of (30-y) MHz. The case completed in NaCl is the (100) interaction plane with longitudinal propagation down a [100] axis. The transverse waves are polarized perpendicular to the mixing plane. The data analysis has not yet been carried out for the NaCl but has been re-analyzed in terms of the ratio of conversion efficiencies for the two polarization cases in fused silica. This procedure gives the third-order elastic constants, A and B, directly and involves less uncertainty by cancelling out the interaction volume. The results for fused silica turn out to be

$$A \simeq -5.27 \times 10^{11} \text{ dynes/cm}^2$$

and

$$B \simeq +5.42 \times 10^{11} \text{ dynes/cm}^2$$

as compared to the results of Bogardus by another method:

$$A = -4.4 \pm 1.2 \times 10^{11} \text{ dynes/cm}^2$$

$$B = +9.3 \pm 0.8 \times 10^{11} \text{ dynes/cm}^2$$

It is clear that the values of A are in agreement. Whether the difference

in the values of B is significant is at present not know as meaningful error intervals for the present work have not as yet been determined.

The second NaCl disc has been oriented by x-rays and measurements of mode mixing for the (100) interaction plane with longitudinal propagation down a [110] axis are now underway. Here again the transverse waves are polarized perpendicular to the mixing plant.

## LOW TEMPERATURE MAGNETIC PROPERTIES OF DILUTE ALLOY SYSTEMS

Senior Investigator: M. P. Maley

The study of the magnetic behavior of very dilute concentrations of magnetic impurities embedded in non-magnetic metallic hosts will be pursued through the use of a Mössbauer effect spectrometer. Since the magnetic hyperfine field acting upon a radioactive nucleus is proportional to the magnetization of the local environment, a measurement of the hyperfine splitting of the Mössbauer spectrum will yield information on the microscopic behavior of local magnetic centers as opposed to the macroscopic averages given by susceptibility techniques. A constant acceleration Mössbauer drive system has been constructed and calibrated. At present, $Fe^{57}$ linewidths, $\Gamma < .3$ mm sec have been obtained with a $Pt/Co^{57}$ source and $K_4Fe(CN)_6 \cdot 3H_2O$ absorber combination. Design and construction have been commenced on a constant temperature cryostat for the source operating continuously between the ranges $1.2^{o}K$ and $300^{o}K$. Studies will be made in magnetic fields supplied by a superconducting solenoid from 0-60 kOe. The primary aim of this investigation is the study of the low temperature anomalies associated with the Kondo effect in dilute alloy systems. The local magnetic moment has been seen to

gradually disappear below a characteristic temperature in many alloy systems. A systematic study on several alloy systems of the effects of large magnetic fields on this transition is planned.

SEMI-CONDUCTION IN GLASS

Senior Investigator: R. K. MacCrone

A series of PbO - $SiO_2$ glass specimens containing .1 to 10 mole per cent $Fe_2O_3$ has been prepared. It has been found that a very pronounced dielectric relaxation occurs in these glasses after being heat treated at 400°C for some hours in a reducing atmosphere. The dielectric relaxation, which occurs at temperatures 260°K, is also mechanically active, and it has been established that the structural entity is confined to a surface layer presumably due to incomplete reduction. The critical experiment using a specimen containing no iron is imminent. Should the relaxation prove due to iron ions, present concepts on the ionic co-ordination in glass will have to be modified.

# ENVIRONMENT SENSITIVE BEHAVIOR

# ENVIRONMENT SENSITIVE BEHAVIOR

Research on corrosion and stress-corrosion of alloys is being conducted in an effort to understand and alleviate phenomena leading to premature failure in agressive environments. Metallic composite alloys, including fiber reinforced metals, duplex stainless steels and cemented carbides, have been shown to corrode at a rate dependent upon the specificity of the environment and the nature of the galvanic interactions between dissimilar phases.

Active study of the feasibility of powering cardiac pacemakers by long-life batteries which use body fluids as an electrolyte is proceeding. Laboratory experiments have been carried out to compare the efficiencies and other characteristics of various anode materials.

A recently completed study of stress corrosion in single-phase copper-base alloys revealed the importance of both metallurgical structure and solution chemistry on the type of cracking and the time to failure. Efforts are now being devoted to varying metallurgical structure in magnesium base alloys be means of precipitation. Stress corrosion experiments are then to be performed with widely differing second-phase particle types and sizes present with the object of optimizing resistance to stress corrosion in a variety of environments.

CORROSION OF COMPOSITES

Senior Investigator: N. D. Greene

The aim of this study is to determine the corrosion and electrochemical characteristics of metallic composite structures. Included in this program are (1) filament reinforced metals, duplex stainless steels (ferrite + austenite) and cemented carbides. Conventional corrosion tests together with controlled potential weight loss measurements and potentiostatic polarization techniques have been utilized.

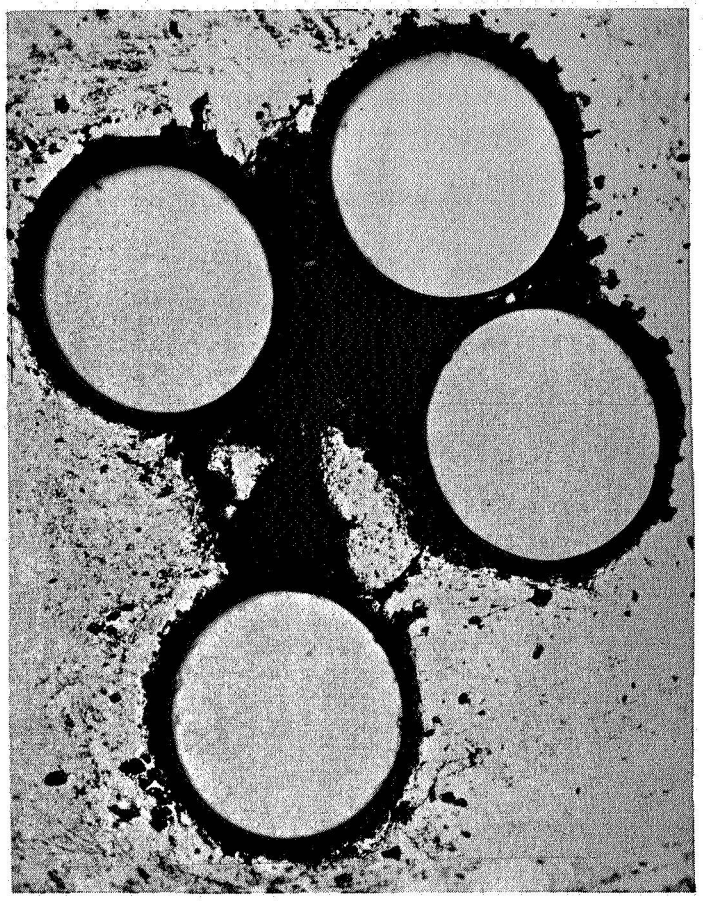
The corrosion behavior of a metal-metal composite is determined by the specificity of the corrosive environment and galvanic interactions between dissimilar metal phases. In the case of metal-metal filament composites, either component may be selectively dissolved depending on the contacting electrolyte. Preferential attack of the filaments is very undesireable since such corrosion is both rapid and difficult to detect and is likely to cause catastrophic failure. An example is shown in Figure 8. Galvanic effects, when present, tend to produce additional corrosion damage as shown in Figure 9.

Selective corrosion of multiphase alloys is a continuing problem. Such alloys are theoretically and experimentally identical to metal-metal fiber composites. Using potentiostatic methods, it has been possible to precisely determine the exact environmental conditions necessary to cause selective corrosion of ferrite in cast stainless steels. If the ferrite phase is continuous, rapid, destructive penetration of the alloy occurs (Figure 10).

Reports summarizing the corrosion characteristics of fiber reinforced metals and duplex stainless steel are currently being

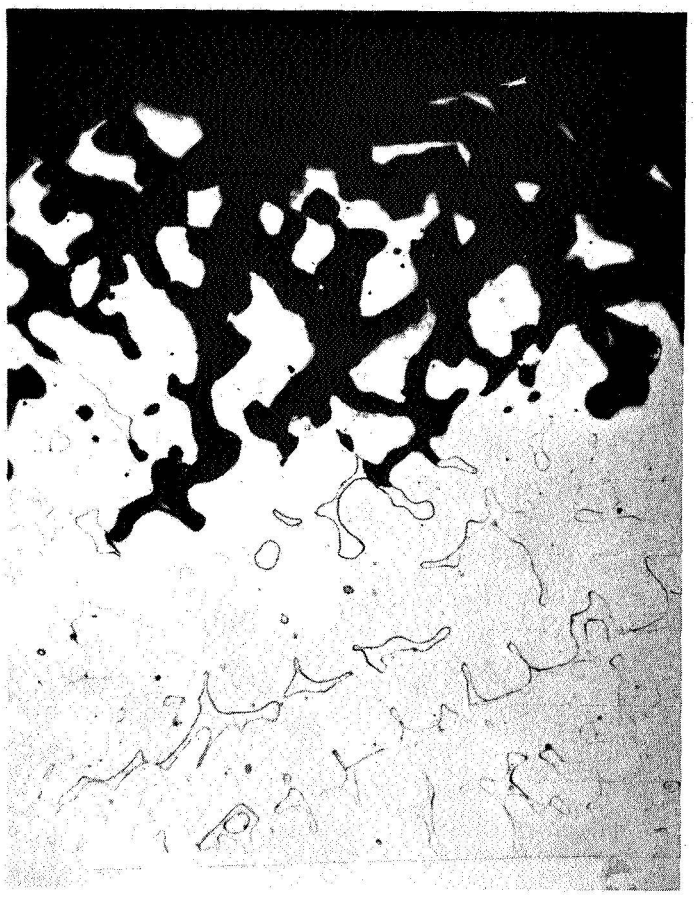
Nickel-tungsten filament composite after 6 days exposure to an oxidizing aklaline solution at room temperature. Longitudinal section showing complete filament dissolution (150x)

FIGURE 8



Appearance of a magnesium - stainless steel (AFC-77) filament composite after exposure to 2% oxalic acid solution. Intense, galvanic corrosion of magnesium evident at wire interface (150x)

FIGURE 9



Selective attack of ferrite in CF-8 cast stainless steel after 3 days exposure to $\bar{N}$ sulfuric acid at -0.4 volt vs saturated calomel reference electrode (150x)

FIGURE 10

prepared. Work on cemented carbides is continuing together with further studies of other fiber composites (e.g. Aluminum-boron).

IN VIVO ELECTROCHEMICAL POWER SOURCES

Senior Investigator: N. D. Greene

The aim of this investigation is to determine the feasibility of powering cardiac pacemakers and other internal devices by long-life, bio-galvanic batteries. That is, batteries which use body fluids as an electrolyte. *In vitro*, laboratory experiments to determine power output, electrode efficiency, and electrochemical characteristics have continued. Previously, it was reported that magnesium anodes have the highest output. However, they are the least efficient (less than 1 per cent), as shown by measurements now in process. The efficiencies of other anode materials vary widely -- from approximately 10 per cent for zinc to nearly 100 per cent for aluminum at high current densities.

*In vivo* experiments have not yet commenced due to design changes in the radio telemetry system to further reduce its size. Several units are now being assembled.

STRESS CORROSION CRACKING OF MAGNESIUM-BASE ALLOYS

Senior Investigator: N. S. Stoloff

A new program has been started to investigate the effects of metallurgical structure upon the susceptibility of magnesium-base alloys to stress corrosion cracking. The two alloys chosen for initial study are Mg-3.7w%Th-0.4%Zr and Mg-0.6%ZR. The structures of these alloys after solution treatment and aging at various temperature have been

determined. Tensile tests are to be conducted in air and in $NaCl-H_2O_2-H_2O$ solutions of varying proportions to determine the effect of these environments on tensile strength and ductility of the alloys in various heat treatment conditions. Dead-load tests also are to be run at various stress levels to establish stress corrosion characteristics.

# TECHNICAL PAPERS SUBMITTED FOR PUBLICATION

# MEMBERS OF FACULTY COMMITTEE ON INTERDISCIPLINARY MATERIALS RESEARCH

# PERSONNEL LIST

## TECHNICAL PAPERS SUBMITTED FOR PUBLICATION

Billmeyer, Jr., Fred W., Marcus, Robert T.
"Effect of Illuminating and Viewing Geometry on the Color Co-ordinates of Samples with Various Surface Textures"
Submitted to Applied Optics

Billmeyer, Jr., Fred W., Katz, Ilan
"Gel Permeation Chromatography of Linear Aliphatic Polyesters"
Submitted to Macromolecular Reviews

Billmeyer, Jr., Fred W., Eckard, Alan D.
"Synthesis of Linear Aliphatic Polyesters"
Submitted to Macromolecular Reviews

Billmeyer, Jr., Fred W., Johnson, G. W., Kelley, R. N.
"Evaluating Dispersion in Gel Permeation Chromatography I. Theoretical Analysis"
Published in Journal of Chromatography, Vol. 3388, 34 (1968) 316-321

Billmeyer, Jr., Fred W., Kelley, R. N.
"Evaluating Dispersion in Gel Permeation Chromatography II. The Injection-Detection System"
Published in Journal of Chromatography, Vol. 3389, 34 (1968) 322-331

Billmeyer, Jr., Fred W., Holleran, Peter M.
"Rapid Osmometry with Diffusible Polymers"
Published in Polymer Letters, Vol. 6 (1968) 137-140

Billmeyer, Jr., Fred W., Kelley, R. N.
"Axial Dispersion of Polymer Molecules in Packed Beds of Non-Porous Glass Beads"
Submitted to Analytical Chemistry

Billmeyer, Jr., Fred W.
"Metamerism - An Introduction"
Published in Color Engineering, Vol. 5, No. 3, May-June 1967

Billmeyer, Jr., Fred W., Smith, Rodger
"Optimized Equations for MacAdam Color Differences"
Published in Color Engineering, November-December 1967

Billmeyer, Jr., Fred W.
"The Look and Think Steps in the Analysis of Color"
Published in the Journal of Paint Technology, Vol. 39, No. 509, June 1967

Billmeyer, Jr., Fred W., Abrams, R. L., Davidson, J. G.
"Color and Appearance Properties of Paint Films"
Published in the Journal of Paint Technology, Vol. 40, No. 519, April 1968

Billmeyer, Jr., Fred W.
"Precision, Accuracy, and Validity of Instrumental Color Measurement"
Published in Journal of Paint Technology, Vol. 38, No. 503, December 1966

Billmeyer, Jr., Fred W., Hobbs, Stanley Y.
"Crystal Unit Cell Dimensions and Densities of Linear Aliphatic Polyesters"
Submitted to Journal of Polymer Science

Billmeyer, Jr., Fred W.
The 1968 Mattiello Lecture "Molecular Structure and Polymer Properties"
Submitted to Journal of Paint Technology

Billmeyer, Jr., Fred W., Livesey, P. J., Fiel, R. J.
"Light Scattering from Microbiological Particles"
Submitted to Applied Optics

Casabella, P. A., Oja, T.
"$B^{11}$ Quadrupole Coupling Constants in Solid Boron Halides"
Submitted to Journal of Chemical Physics

Lenel, F. V., Ansell, G. S., Gessinger, G. H.
"Estimate of the Temperature Rise of Micron-Sized Silver Particles in the Electron Microscope due to Electron-Beam Heating"
Published in Journal of Applied Physics, Vol. 39, No. 12, November 1968, 5593-5597

Lenel, F. V., Ansell, G. S., Gessinger, G. H.
"Continuous Observation of the Sintering of Silver Particles in the Electron Microscope"
Published in Transactions Quarterly, Vol. 61, No. 3, September 1968

Lenel, F. V., Ansell, G. S., Singh, M.
"The Plastic Deformation of Internally Oxidized Silver-Magnesium Single Crystals"
Published in Supplement to Transactions of the Japan Institute of Metals, Vol. 9 (1968)

Stoloff, N. S., Mushovic, J. N.
"Precipitation Hardening of a Mg-Th-Zr Alloy"
Published in Supplement to Transactions of the Japan Institute of Metals, Vol. 9 (1968)

Stoloff, N. S., Blackwood, A. W.
"The Mechanism of Stress Corrosion Cracking in Cu-Al Alloys"
Submitted to Transactions of the American Society of Metals

Wiedemeier, H., Khan, A.
"Phase Studies in the System Manganese Sulfide-Cadmium Sulfide"
Published in Transactions of the Metallurgical Society of AIME, Vol. 242, September 1968

Wunderlich, B., Jaffe, M.
"Superheating of Extended-Chain Polymer Crystals"
Submitted to the Proceedings of the Second International Conference on Thermal Analysis, Worcester, Mass.

Wunderlich, B., Jones, L. D.
"Heat Capacities of Solid Polymers"
Submitted to Journal of Macromolecular Science - Part B

Wunderlich, B.
"Heat Capacities of Linear High Polymers"
Submitted to Advances of Polymer Science

Wunderlich, B., Prime, R. Bruce, Melillo, Louis
"Extended Chain Crystals V. Thermal Analysis and Electron Microscopy of the Melting Process of Polyethylene"
Submitted to Journal of Polymer Science

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