MAY 6 1965

GENERAL ATOMIC

DIVISION OF **GENERAL DYNAMICS**

MASTER

AEC RESEARCH AND
DEVELOPMENT REPORT

GA-5734

A PROGRAM OF BASIC RESEARCH ON MECHANICAL
PROPERTIES OF REACTOR MATERIALS

ANNUAL SUMMARY REPORT
FOR THE PERIOD ENDING OCTOBER 31, 1964

Prepared under
Contract AT(04-3)-167
Project Agreement No. 4
for the
San Francisco Operations Office
U.S. Atomic Energy Commission

PATENT CLEARANCE OBTAINED. RELEASE TO
THE PUBLIC IS APPROVED. PROCEDURES
ARE ON FILE IN THE RECEIVING SECTION.

January 15, 1965

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

GENERAL ATOMIC
DIVISION OF
GENERAL DYNAMICS

JOHN JAY HOPKINS LABORATORY FOR PURE AND APPLIED SCIENCE

P.O. BOX 608, SAN DIEGO, CALIFORNIA 92112

AEC RESEARCH AND
DEVELOPMENT REPORT

GA-5734

A PROGRAM OF BASIC RESEARCH ON MECHANICAL
PROPERTIES OF REACTOR MATERIALS

ANNUAL SUMMARY REPORT
FOR THE PERIOD ENDING OCTOBER 31, 1964

Prepared under
Contract AT(04-3)-167
Project Agreement No. 4
for the
San Francisco Operations Office
U.S. Atomic Energy Commission

Work done by:

R. H. Chambers
H. Harper
W. Flynn
J. Schultz
T. A. Trozera
J. L. White

Report written by:

R. H. Chambers
T. A. Trozera
J. L. White

January 15, 1965

PREVIOUS REPORTS IN THIS SERIES

GA-4900—Summary report of work from October 1,
1962, through September 30, 1963

GA-5340—November, December, 1963; January, 1964

GA-5520—February, March, April, 1964

GA-5620—May, June, July, 1964

ABSTRACT

Transmission electron microscopy of tantalum single crystals deformed to large strains did not show a cell structure unless the deformed crystal was heated in an oxygen atmosphere prior to thinning.

No difference was observed between as-rolled crystals and those given a thermal treatment without oxygen. The results indicate that the oxygen pins the dislocations and/or modifies their structural arrangement. It was not possible to isolate the mechanism.

Tungsten single crystals of very high purity were prepared from vapor-deposited stock by electron-beam floating-zone melting. Additional purification was attempted by solid-state extraction, with inconclusive results, and by electrotransport, which appeared quite successful. The residual resistivity ratio for a crystal grown using electrotransport was about twice that of crystals grown by simple zoning. An indication of true zone refining is also apparent in that the resistivity ratio for the last portion of the crystal to solidify is about one half that of the rest of the crystal. The specimens produced have an impurity level near or below the limits of detection by chemical or spectrographic techniques. Residual resistivity measurements by the potential-drop and eddy-current methods gave ratios in the range of 25,000 to 150,000. The absolute values in the upper range are questionable, however, since the measurements were at the limits of detection of the measuring apparatus. Measurements of proportional limit and work-hardening rate have also been used as an indication of relative purity.

Two tungsten specimens cut from one single crystal are currently being irradiated and will be used for experiments on the recovery of yield strength and resistivity with annealing.

The methods of acoustical spectroscopy and high-amplitude modulus-defect measurements applied to the study of the mechanical state of a metal have provided unique insight into the underlying mechanisms that control plastic deformation in the refractory bcc metals over ranges of purity, strain rate, stress, and temperature.

From the studies it appears that the motion of dislocations in the bcc transition metals is controlled by thermally activated processes possessing an energy spectrum with a number of broad bands. There is evidence that the activation energy of some of these bands may be reduced by the application

of stress, i. e., that the thermal activation event may be stress-assisted. Furthermore, the highest energy process appears to possess the largest rate of energy reduction by stress or activation volume.

The knowledge of the existence of many components in the network, each with its particular mobility and stress concentration factor, provided the original incentive for the construction of a model of stress-assisted, thermally activated, dislocation motion that is now being investigated.

Measurements of the stored-energy release on annealing specimens of irradiated and cold-worked molybdenum are in progress, using specimens supplied by Hanford Laboratories. Two important release peaks were found in the irradiated specimens, in the vicinities of 200°C and 700°C, and the more highly irradiated specimens show possibilities for additional annealing peaks. Data reduction is in progress and a topical report will be prepared.

CONTENTS

I.	DEFORMATION MECHANISMS IN BCC METALS	1
1.1.	Transmission Microscopy	1
1.2.	Irradiation Effects in bcc Metals	12
1.2.1.	Material	13
1.2.2.	Material Characterization	23
1.2.3.	Evaluation of Source Materials	29
1.2.4.	Tungsten Irradiation	37
II.	DISLOCATION DYNAMICS	46
2.1.	Models of Dislocation Relaxations in bcc Transition Metals	47
2.1.1.	Dislocation Relaxation Versus Point-defect Relaxation	47
2.1.2.	Model of Stress-amplitude and Temperature-dependent Dislocation Motion in bcc Transition Metals	49
2.1.3.	Mechanisms Which Determine Mobility of Dislocations	65
2.2.	Discussion of Experimental Results and Models of Dislocation Relaxations in bcc Transition Metals	71
2.2.1.	Dislocation Relaxation Activation Energy Spectrum	71
2.2.2.	Conditions Necessary for Observation of Dislocation Relaxations	72
2.2.3.	Comparison of Hasiguti and Bordoni Peaks in fcc Metals with Deformation-induced Peaks in Refractory bcc Metals	73
2.2.4.	The Significance of Aging Phenomenon	77
2.2.5.	Discussion of Amplitude Dependence	81
2.3.	Conclusions and Suggestions for Further Investigation	84
III.	STORED-ENERGY RELEASE IN IRRADIATED MOLYBDENUM	90
3.1.	Experiments	90
3.2.	Results	91

I. DEFORMATION MECHANISMS IN BCC METALS

1.1. TRANSMISSION MICROSCOPY

During the course of the present work, transmission electron microscopy of deformed tantalum single crystals was performed. A number of interesting and significant observations were made and have been reported previously.^{(1)*} It is the purpose here to present only the most pertinent portions of the work, which may also serve in part as a summary.

A number of samples were prepared and inspected by transmission electron microscopy. The samples were all prepared in a similar manner and with a similar background; i.e., all specimens were originally single crystals of tantalum having had one zone melting pass, and were rolled to approximately 90% reduction area. Following the rolling treatment, samples were electrolytically thinned by standard methods in order to make them transparent to electrons. One set of experiments deviated from this procedure in that the samples were given different heat treatments in order to evaluate pinning effects.

Many of the observations made on unpinned samples were similar in nature to those made by other investigators,⁽²⁾ i.e., a number of tangles were found and many prismatic loops were also in evidence (Fig. 1). However, these features have usually been found at low strain values. Various models have been proposed to explain the presence of prismatic loops, and their observation here simply supports previous studies. Several aspects of this early portion of the work, however, were at variance with other studies. Principal among these was the pronounced lack of cell structure following very large deformations. Cell structure appears to be characteristic of deformation and has been observed and reported for both fcc metals⁽³⁾ and bcc metals.⁽²⁾ Keh and Weissman⁽²⁾ performed a systematic study of the influence of temperature and deformation on the dislocation structure in iron and found that the formation of cells was a function of both deformation and temperature.

Two features of the present work were different from other studies: (1) the deformations were rather high (90%) and (2) the stress-strain curves for the tantalum crystals used exhibited a very low rate of work hardening ($d\sigma/d\epsilon = G/1500$) compared with the typical rate ($d\sigma/d\epsilon = G/630$) for the iron crystals used by Keh and Weissman.

*References are listed at the end of each section.

P-2073

(215,80×)

Fig. 1--Typical transmission photomicrograph
of as-rolled tantalum single crystal

The absence of cell structure in the early work was notable in view of other observations on both fcc and bcc metals where cell formation was always seen with deformation. As a result, pinning experiments were undertaken to find an explanation. One tentative explanation offered for the lack of cells in the early work was simply that the dislocations were able to rearrange themselves during the thinning process. The image forces⁽⁴⁾ seen by dislocations during thinning have been proposed as the cause of the rearrangement. These image forces purportedly approach a fraction of the shear modulus for the material. The first experiment to evaluate this effect was to anneal a foil in air at 400°C for eight hours before thinning. This temperature and time were calculated to be sufficient to introduce oxygen throughout the sample. Figure 2a is a photomicrograph of one area observed. It can be seen that this structure is quite different from that of Fig. 1 in that a cell structure is now in evidence. Figure 2b is a selected area diffraction photomicrograph of this area and shows the misorientation between subgrains to be as large as 4° to 5°. It was not possible in this sample to find areas where only sharply defined spots were present; rather, a spreading of the spots was usual, indicating a range of orientations of the subgrains.

The first thermal treatment provided an indication of the changes caused by oxygen and/or temperature, but did not, of course, define these effects. The 400°C temperature used for the first annealing treatment is considered to be too low to have caused the rearrangement of the dislocations as seen. A possible explanation, however, lies in a suggestion by Lothe⁽⁵⁾ that the presence of an impurity atmosphere in itself could cause a rearrangement of the dislocations. Final experiments were performed in an effort to evaluate these variables. A single crystal of tantalum was rolled to ~90% reduction of thickness and sectioned into three pieces. Two of these sections were placed in quartz ampoules, one filled with oxygen, the other with argon. The two quartz ampoules were then given a 400°C thermal treatment for eight hours. The third section was used as a reference for comparison.

The results of transmission microscopy on the three samples are presented in Figs. 3 through 5. The four photomicrographs making up each figure were selected to represent the most widely divergent structures observed and should form a valid basis for comparison. Figure 3, showing transmission photomicrographs of the as-rolled crystal, is typical in that it presents examples of most of the features previously seen on as-rolled crystals. Figure 4, showing the specimen annealed in argon, shows, with few exceptions the same general features as seen in Fig. 3. Photomicrographs of the sample annealed in oxygen are presented in Figs. 5 and 6. Figure 5 was compiled on the same basis as Figs. 3 and 4; that is, the most widely divergent observations were selected. Figure 6 shows one area taken at three different tilt angles and identifies the boundaries as such.

P2309

P2310

Fig. 2--Transmission electron photomicrograph of rolled tantalum single crystal after thermal treatment to pin dislocations, with selected area diffraction

P-2644

(45,000×)

(a)

P-2639

(33,060×)

(b)

Fig. 3--Transmission photomicrographs of as-rolled tantalum single crystal.

P-2074

(c)

(34,800×)

P-2643

(d)

(33,060×)

Fig. 3 (continued)--Transmission photomicrographs of as-rolled tantalum single crystal

P-2630

(a)

(34,200×)

P-2631

(b)

(33,060×)

Fig. 4--Transmission photomicrographs of rolled tantalum crystal, annealed 8 hr at 400°C in argon

P-2631

(c)

(70,000×) P-2634

(d)

(31,920×)

Fig. 4 (continued)--Transmission photomicrographs of rolled tantalum crystal annealed 8 hr at 400°C in argon

P-2714

(a)

(54,000×) P-2729

(b)

(52,200×)

Fig. 5--Transmission photomicrographs of rolled tantalum crystal annealed 8 hr
at 400°C in oxygen

P-2694

(c)

(57,000×) P-2311

(d)

(54,000×)

Fig. 5 (continued)--Transmission photomicrographs of rolled tantalum crystal annealed 8 hr at 400°C in oxygen

Fig. 6--Transmission photomicrograph of rolled tantalum crystal annealed 8 hr at 400°C in oxygen

The results on the sample annealed in oxygen can be seen to support those obtained from the first sample annealed in air in that well-developed subgrains are present. The lack of this structure for the sample annealed in argon would indicate that the effect of the thermal treatment per se does not significantly change the structure. These observations do not support or reject the model proposed by Lothe⁽⁵⁾; however, in the process of pinning dislocations in order to avoid their loss during thinning, modification to the observed structure is a distinct possibility and should be seriously considered.

1.2. IRRADIATION EFFECTS IN BCC METALS

Many studies have been performed on the effects of neutron damage in metals. These studies can be broadly classified into two categories. A very important part of the studies has been concerned with the gross effect of neutron damage on reactor structural materials, and these results have obvious and immediate engineering use. A second category has dealt mainly with the effects of irradiation on pure metals, and the primary objective has been to define the mechanisms of various kinds of damage caused by high-energy particles. Experiments of this nature can be classified as fundamental in purpose, since the aim is to try to understand the kinds of damage to the crystalline lattice on an atomic scale caused by various types of particles. Much work has been done in the past to evaluate the effects of neutron damage in pure fcc metals. The effects of neutron damage in bcc metals, however, are not as well understood. A significant reason for this is felt to be that relatively pure fcc metals can be obtained more easily than bcc metals. It has been the objective of this program to study the effects of neutron damage to bcc metals of such high purity that the likelihood of interactions between point defects produced during irradiation with interstitial atoms present as impurities would be negligibly small. An additional factor overcome with ultra-high-purity starting material is that it has, in the past, been difficult to evaluate irradiation effects per se because interstitial atoms, such as carbon, nitrogen, and oxygen, are thought to affect mechanical properties in a similar manner, thus obscuring the effects of neutron damage, particularly at low doses. For this reason, major past emphasis has been placed on producing an ultra-pure starting material and characterizing it by all the means available. The methods used to produce and characterize ultra-pure tungsten for the initial studies are described in this section.

The presence of foreign atoms has been known for some time to influence measurements of both mechanical⁽⁶⁾ and electrical⁽⁷⁾ properties. Calculations by Damask⁽⁸⁾ indicate that impurity levels as low as 10^{-7} are necessary to ensure that measurements of annealing kinetics of vacancies in bcc metals are not influenced by the impurity-vacancy interactions.

A number of experiments have shown the effects of impurities on recovery of resistance during postirradiation annealing.⁽⁷⁾⁽⁹⁾

The rate of disappearance of carbon from solution in iron due to irradiation is about three orders of magnitude greater than the thermal rate as reported by Damask.⁽¹⁰⁾ One also is tempted to ascribe the many different results obtained by investigators measuring property changes due to irradiation, at least in part, to the influence of foreign atoms.

The experimental program planned to elucidate the mechanisms of irradiation damage in ultra-pure tungsten includes (1) measurements of the increase of critical shear stress with neutron dose and its recovery with annealing, (2) measurements of the recovery of electrical resistance of irradiated specimens with postirradiation annealing, (3) stored-energy measurements (presently in progress on irradiated molybdenum in cooperation with Hanford Laboratories), and (4) internal friction measurements.

The methods used to obtain and characterize the starting material will be described in detail, but can be summarized briefly. Starting material is presently prepared by high-vacuum floating-zone refining, very recently in combination with electrotransport in the liquid state during zoning. Characterization of the material is considered of utmost importance and is presently being done by residual resistivity measurements, measurements of the proportional limit and early strain hardening characteristics, and internal friction measurements. The latter can, by means of strain amplitude measurements, provide invaluable information concerning the structural state of the material.

1.2.1. Material Preparation

1.2.1.1. Electron-beam Floating-zone Refining. Since an important program objective is to perform experiments on specimens of maximum purity, electron-beam floating-zone refining was used as a means of preparing single crystals for the studies. Other methods that have been or are presently being used to further purify the crystals will be described; however, zone refining was the first method used and remains the primary method of specimen preparation. An excellent coverage of the principles involved in growing crystals by this method is presented by Pfann,⁽¹¹⁾ and only the details pertinent to the present work will be described here. The interstitial impurity atoms, such as nitrogen, oxygen, and carbon, are thought to have a great effect on the properties of tungsten, and their removal by zone refining in normal vacuums ($\sim 10^{-6}$ torr) is far from complete.⁽¹²⁾ It was felt that a system pressure of $\sim 10^{-9}$ torr during zoning would largely effect removal of many impurities through volatilization. Recent results by Murray, et al.,⁽¹³⁾ have since shown a great effect of pressure on residual resistivity ratio (see Fig. 7). Removal of carbon seems to occur

Fig. 7--Variation of resistance ratio with chamber pressure for one pass float-zoned tungsten at 4 in./hr (from Ref. 13)

mostly through its reaction with oxygen to form CO or CO₂⁽¹⁴⁾ and, largely for this reason, a starting material of initially low carbon content was sought.

The main parameters used as a basis for designing and building the zone refining system were (1) that the vacuum system itself should contribute minimum impurities during operation and (2) that the components of the traverse system (electron gun, etc.), which are contained within the vacuum system during zoning, should be made of low-vapor-pressure components. An all-metal bakable system that satisfies the minimum gas-load requirement has a total cycle time measured in days. An elastomer-sealed metal or glass system has a total cycle time measured in hours, especially if high-speed pumping is used to overcome the higher gas load during zoning. For these reasons, a parallel development was started on the two types of systems. One was an all-metal bakable system with a 125-liter/sec ion pump. This system was expected to produce the cleanest and best vacuum and was planned as the ultimate system. It was felt that the high vacuum would warrant the large amount of time involved in a complete cycle. A second system with a glass chamber of standard 6-in. Pyrex pipe was designed to provide good visibility of the working chamber and quick cycle time. This system was built mainly to provide a simple means of evaluating electron gun designs and other internal components. It is also used for welding of end grips to specimens. The high pumping speeds needed were provided by a 750-liter/sec oil diffusion pump and liquid nitrogen cold trap. This combination had a blank-off pressure in the 10^{-10} torr range.

The requirement of low-vapor-pressure components in the system is best met by eliminating all oils, plastics, etc., and using only stainless steel, copper, tantalum, etc. The elimination of lubricants and plastics posed a problem because relative motion between the specimen and electron gun is necessary to provide the zone motion. In tests performed at a chamber pressure of $\sim 10^{-5}$ torr, various vacuum greases and oils were found to provide sufficient lubrication at the low speeds (~ 2 mm/min) involved. At ultra-high vacuums ($\sim 10^{-9}$) they were found unsuitable, especially when the system was baked out. To provide alignment of the specimen and the electron gun within the vacuum system, guides and a means of moving one component were needed. A magnetically coupled rotary drive was designed and built for this purpose. This required that a rotary-to-linear motion conversion be made within the vacuum system. A ball screw and nut were chosen for this purpose because of the low operating force and minimum contact area between components. Molybdenum disulfide was known to retain its lubricating properties under conditions of high vacuum and high temperature ($\sim 450^\circ\text{C}$), and was considered for use. A molybdenum disulfide coating was applied to the ball screw and the system was cycled in a vacuum of 10^{-6} torr at $\sim 200^\circ\text{C}$, with no adverse effects. However, alignment problems in the traverse mechanism proved difficult to overcome and the entire mechanism was replaced with a stainless steel bellows having an 8-in. linear travel.

The glass system used elastomer seals, and a differentially pumped Wilson-type seal was used to transmit vertical motion into the system. This was found to work satisfactorily at linear speeds of ~ 2 mm/min. Pressure in the system could be maintained at $\sim 8 \times 10^{-9}$ torr with this seal. In both systems Type 304 stainless steel was used for all internal components except for current conductors (copper), insulators (alumina and Kovar), and portions of the electron gun that operate at temperatures of 600° to 700° C. The Mark I electron gun was formed largely of tantalum, with a tungsten wire filament (see Figs. 8a and 8b). The Mark I gun had excellent focusing properties, and a 1-mm-diameter tantalum rod was successfully zoned. However, the molten zone of the specimen lies completely within the enclosed bias shroud and the conductance to the vacuum chamber was considered inadequate. The second design, shown in Fig. 8c, provided very good conductance to the chamber and produced specimens of improved purity as evidenced by measurements of the proportional limit. Focusing is adequate to maintain a zone in specimens 1.5 to 2 mm in diameter. This gun is also used to weld molybdenum end grips to the tungsten specimens (see Fig. 9). Figures 10a and b show the specimen support with a specimen in place, the Mark II gun, the gun support, and the high-current lead wires for electrotransport.

Experience with both systems soon indicated that insufficient pumping speed was available to achieve vacuum levels of 10^{-9} torr during zoning. The chamber walls are cooled by water jackets or tubes and forced air to help decrease outgassing, but this is still considered a large part of the total gas load. Titanium sublimation pumping has been used in many applications and appears to be well suited for handling the large amounts of active gases resulting from outgassing of hot chamber walls and internal components.

Figure 11 is a drawing of a small (area ~ 80 cm²) titanium sublimation pump that was built and installed in the glass vacuum system. Several types of filaments were tried; however, wires made of an alloy of tantalum and titanium were most reliable. These filaments can be heated to above the melting point of titanium with greatly increased rates of titanium vaporization and hence increased deposition on the tantalum wall. Considerable success was obtained using this small sublimation pump, and vacuums of 5×10^{-8} torr have been attained during zoning. This system is limited owing to heating of the tantalum wall by the filament. For this reason a decision was made to incorporate a liquid-nitrogen-cooled cold wall into the zoning chamber. It is planned that most of the cold wall will be used as a pump as a result of direct deposition of titanium on the wall. This modification to the system should reduce the system pressure to $\sim 10^{-9}$ torr during zoning. This pressure range is felt to represent the approximate limit at which vacuum distillation of impurities can be accomplished.

(a)

(b)

(c)

Fig. 8--(a) Mark I electron gun; (b) schematic drawing of Mark I electron gun; (c) schematic drawing of Mark II electron gun

Fig. 9--Tungsten specimen welded to molybdenum end grips

1.2.1.2. Solid-state Purification. During the portion of the program when all available methods of improving the purity of existing starting material were being considered, solid-state purification was included. In view of existing work, it appeared that use of this method might possibly effect removal of interstitial impurities from bcc metals. Seraphim, et al., ⁽¹⁵⁾ performed an excellent study of the use of this method to purify small-diameter (0.25 mm) tantalum wires. They reported values for Γ , the helium temperature resistance ratio, in excess of 10^4 . If one utilizes the conversion figures of Seraphim, et al., ⁽¹⁶⁾ i.e., atomic-percent interstitial content $c \cong 2.7 (1/\Gamma)$, an interstitial content of $\sim 2.7 \times 10^{-6}$ atomic results. Tantalum wires of small diameter have also been purified, using the same concepts, at General Atomic. Resistivity ratios as high as 6500 have been obtained.

The application of this method to tungsten for carbon removal was considered. Work of Becker, et al., ⁽¹⁴⁾ showed that the reaction of oxygen with carbon in tungsten to produce CO and CO₂ reached a maximum rate at $\sim 2300^\circ\text{K}$. An obvious disadvantage is that if carbon were present, it would have to be redistributed many times in order to react with oxygen at the surface. This limits the technique to thin foils or small-diameter wires, neither of which is suitable for the planned irradiation experiments.

Solid-state purification was attempted on a sample of ~ 1.5 -mm diameter (TH-7) utilizing five temperature cycles to within 200°C of the

Fig. 10--(a) Specimen support with specimen in place, the Mark II gun, the gun support, and high-current lead wires for electrotransport

Fig. 10 (continued)--(b) Mechanical schematic of the electron-beam zoner

Fig. 11--Titanium sublimation pump

melting point of tungsten, with each cycle followed by an exposure to an oxygen partial pressure of 10^{-6} torr at 2300°K . The pressure during the high-temperature cycles was 8×10^{-9} torr. This experiment was performed in the all-metal system. Resistivity measurements before and after were identical ($\sim 23,000$), which indicates that the results are inconclusive. This could be caused by the large sample size and/or low carbon content. It does not, at present, appear practical to consider this method for the sample sizes required (~ 2 mm), although a recently suggested method could be used to effectively redistribute any carbon present. This method would consist of a zone pass which quite effectively stirs the molten zone, hence redistributing the carbon, followed by exposure to oxygen at $\sim 10^{-6}$ torr and 2300°K . In view of very recent work to be described in the following section, it appears that the method of electrotransport in the liquid state may be more useful for our purpose.

1.2.1.3. Electrotransport. The use of an electric field to effect mass transport of metal ions in both the liquid and solid state is well known, and a recent review by Verhoeven⁽¹⁷⁾ summarizes both past work and theoretical features. Electrotransport, in the solid state, has been shown to be quite effective in moving impurity atoms, and an excellent example is the work of DeBoer and Fast,⁽¹⁸⁾ who studied migration of oxygen in zirconium. They found that under suitable conditions of temperature and electric field, oxygen could be made to move easily through the metal lattice as a negative ion. The fascinating aspects of electrotransport lie in the application of this method to the molten state where diffusion rates are greatly accelerated.

Angus, et al.,⁽¹⁹⁾ derived a steady-state solution for the segregation occurring at a freezing interface for the case of an added electric field and predicted that increases in segregation could be quite large under certain experimental conditions. Pfann and Wagner⁽²⁰⁾ later derived a general relationship for the effective distribution coefficient k when a direct current is passing through a solid-liquid interface. It was shown that k could be varied over wide ranges between k_0 (the equilibrium value) and unity. It was shown, as a consequence, that increased efficiency of zone refining could result from changes in the distribution coefficient k . Some recent experimental results⁽²¹⁾ confirmed these concepts for tungsten. The method used to evaluate the changes during zone refining caused by an added electric field was measurement of the residual resistivity ratio Γ , and some striking improvements were reported. Although no analyses for changes in carbon content were indicated, molybdenum was shown to concentrate at one end, and the average molybdenum content was reduced from 20 ppm to 5 to 6 ppm for an electric field intensity of 1000 amp/cm^2 . Field-aided zone refining (field freezing) has been performed on vapor-deposited starting material presently being used, and some preliminary results will be presented. The circuit used is essentially the same as that

used by Hay and Scala⁽²¹⁾ (see Fig. 12). Since the original zone-refining apparatus was not planned with this in mind, a standby feedthrough was used and, consequently, the current density was limited to about 850 amp/cm².

Preliminary analysis of a specimen (TH-18) zoned at 2 mm/min and 850 amp/cm² indicated a residual resistivity ratio $\Gamma = 60,000$ over most of the length of the crystal and $\Gamma = 30,000$ in the final 1 cm, which included the last part of the specimen to solidify. It would appear that some true zone refining occurred. These values may be compared with a value of $\Gamma = 22,500$ for a section of TH-7 grown under normal conditions. However, the zone-refining conditions were not identical and the comparison is not completely valid. Resistivity measurements have also been performed on a crystal (TH-16) grown under essentially the same system conditions, but without the electric field. The results are presented in Table 1, and the differences are indeed striking. The resistivity ratios presented in Table 1 for TH-18 were obtained under the same conditions as for TH-16. The decrease in resistivity ratio for the last section of TH-18 to solidify indicates that some true zone refining, in addition to volatilization of impurities, has occurred. The increase in resistivity ratio by about two times for the case of field freezing is considered extremely encouraging; however, caution must be exercised in interpreting the absolute ratios in Table 1. The numbers obtained are close to the limits of detection for the equipment being used and could be in error. The comparison between the two crystals is considered valid, however, and is in approximate agreement with the results of Hay and Scala⁽²¹⁾ under about the same experimental conditions. At 1000 amp/cm², the resistance ratio after one pass was observed to go from $\Gamma = 23,000$ to $\Gamma = 42,000$. Work is continuing on this phase of crystal growth. Measurements of the proportional limit for these crystals will be made and compared with those for crystals grown without the electric field. If improvement in these mechanical properties is also evident, future irradiation capsules will contain crystals grown by this method.

1.2.2. Material Characterization

As previously noted, considerable effort has been placed on methods of obtaining pure starting material and further improving its purity. An immediate problem, of course, arises in how one assesses specimen purity. Chemical analyses are useful as a general guide, but are not of much use in the purity range desired ($<10^{-7}$ impurity concentration). Two methods are presently being used as a regular means of detecting differences caused by changing the conditions under which the crystals are grown: (1) electrical resistance measurements and (2) mechanical property measurements. The first is a well-accepted method that is sensitive to impurities that scatter conduction electrons (mainly interstitial impurity atoms). It consists of measuring the electrical resistance of the sample at room temperature and comparing this with the same measurement at

Fig. 12--Schematic diagram for electrotransport zone-refining process

liquid-helium temperature. A detailed discussion of the theory and ramifications of electrical resistance measurements may be found in books such as that by Olsen.⁽²²⁾ Measurement of resistance ratios has been performed by two methods: (1) the potential-drop method and (2) the eddy-current decay method. The second method of determining relative purity is to measure the proportional limit and the work-hardening rate at small strains. These measurements are termed mechanical property measurements.

Table 1
RATIO Γ OF ELECTRICAL RESISTANCE AT ROOM
TEMPERATURE TO THAT AT 4°K (R_{2980K}/R_{40K})
FOR ZONE-REFINED TUNGSTEN WITH AND
WITHOUT ELECTRIC FIELD^a

Measuring Position	$\Gamma \times 10^{-3}$	
	Without Field (TH-16)	With Field of 850 amp/cm ² (TH-18)
Top	50.9	40.0
	61.6	114.0
	54.4	100.0
Bottom	64.4	151.5

^aZone traverse was bottom to top at 2 mm/min. Top electrode was maintained at positive potential.

1.2.2.1. Potential-drop Method of Measuring Residual Resistivity Ratio. This method of residual resistivity measurement is simple in concept but rather difficult in practice at resistivity ratios greater than about 10,000. For high-purity samples of a size useful for mechanical property measurements, the measured potential drop is of the order of 0.05 to 0.5 μ v at reasonable current levels. When the electron mean free path between impurities is significantly less than the boundary dimensions of the specimens, the potential drop between two points along the path of the constant current flowing axially will be due principally to electron scattering by impurities at temperatures low enough to freeze out most of the thermal lattice vibrations (4.2°K). Residual resistivity Γ is commonly defined as the ratio of potential drop (298°K) to potential drop (4.2°K) at constant current.

The technique employed uses a battery with a series ballast resistor to limit and help maintain constant current (~ 6 amp), a reversing switch to change direction of current flow through the specimen, and a fixture with a low thermal mass and conductivity for immersing the specimen in liquid helium. A 0.0005-ohm precision resistor is placed in series with the circuit to allow current measurement by potential drop. A reversal of current flow is necessary to allow a subtraction of thermal electromotive forces, which are often larger than the potential drops.

The potential drop at selected points on the specimen is obtained by spot-welding 0.003-in.-diameter platinum wire, which is then soldered to copper lead wire. Low-thermal silver contact switches are used to select any two points for potential-drop measurement. When the potential drop is in excess of 1 v, a Leeds and Northrup K3 potentiometer with galvanometer can be used. A Keithly 150A microvolt meter has also been used, and this instrument can detect a potential drop of about $0.05 \mu\text{v}$.

1.2.2.2. Eddy-current Method of Measuring Residual Resistivity Ratio. This method of measuring the resistivity utilizes the decay of flux from a bar situated in an external magnetic field that has been rapidly reduced to zero.⁽²³⁾ Several measurements (courtesy of M. Merriam, University of California at San Diego) have been made on tungsten single crystals, and the ratios obtained were found to be in agreement with those obtained using the potential-drop method. The agreement in this case was not felt to be conclusive, since the decay method was used on an as-grown single crystal of about 1.5-mm diameter and the potential-drop measurement was performed on a specimen of ~ 0.25 -mm diameter that was used for internal friction measurements.

The chief advantage of the decay method is that no electrical connections need be made to the sample. The main limitation is the difficulty of measuring the long decay times and associated low voltages in specimens of high purity.

Figure 13 presents the experimentally obtained decay of voltage with time for a zone-refined tungsten single crystal (TH-7) at 4.2°K . After a relaxation time, shown as t_r on Fig. 13, the voltage approaches a simple exponential of the form

$$V(t) = K \exp(-t/t_r) \quad (1)$$

where t_r , the relaxation time, is

$$t_r = 2.17 \mu R^2 10^{-9} / \rho \quad (2)$$

and t = time,

Fig. 13--Voltage decay with time using eddy-current method for TH-7

ρ = resistivity in ohm-cm,

μ = permeability, ~ 1 in a weakly magnetic material,

R = radius of cross section.

The relaxation time t_r is obtained by taking the derivative of voltage with respect to time (Eq. (1)) and is

$$t_r = 0.434 \frac{\Delta t}{\Delta \log V}.$$

From Fig. 13 we can obtain

$$t_r = \frac{0.434}{2} (273 - 0) = 59 \times 10^{-3} \text{ sec.}$$

Direct substitution of this value of t_r into Eq. (2) with $R = 8 \times 10^{-2}$ cm yields $\rho_{4.2} = 2.35 \times 10^{-4}$ ohm-cm. The resistance at room temperature $\rho_{295} = 5.3 \mu\text{ohm-cm}$,⁽²⁴⁾ and the ratio $\Gamma = \rho_{295}^{\circ\text{K}} / \rho_{4.2}^{\circ\text{K}} = 22,500$.

The resistance ratio for a small (0.25-mm) specimen zoned under similar conditions was found to be $\sim 25,000$. This value may well have been limited by surface scattering.

Bean, et al.,⁽²³⁾ indicate that a limiting resistance of 10^{-11} ohm-cm may be expected for a sample ~ 1 cm in diameter. It is not clear yet whether this limit is due to difficulty of measuring microvolt signals at long relaxation times or to surface scattering.

It has not yet been possible to perform size-effect experiments on samples using the potential-drop method. These experiments are necessary to determine the bulk resistivity and hence the limitation due to surface scattering. A theoretical estimate of the effect of surface scattering will be made. Both methods of measuring the resistance ratio suffer from this shortcoming. Even though measurements of the resistance ratios may approach a limit due to surface scattering, it may yet be possible to detect differences in purity by means of mechanical property changes such as the proportional limit and strain-hardening rate, which are felt to be sensitive to impurities in the form of precipitated clusters. Resistivity measurements do not seem to be sensitive to impurities in this form.

1.2.2.3. Mechanical Property Measurements. The apparent insensitivity of resistivity measurements to impurities in the form of precipitates formed, in part, the basis for using measurements of the proportional limit and strain-hardening rate as an index to crystal purity. These mechanical properties are known to be sensitive to structure and impurities. Strain, as measured by cross-head motion, was considered unsatisfactory for the

required measurements. For this reason, a clip-type extensometer was designed and built, and is shown in place on a specimen in Fig. 14. The sensing elements are resistance-type strain gauges that form two arms of a bridge circuit. The remaining two arms are connected to the circuit at the Sanborn preamplifier, which supplies the exciting voltage and provides a signal to the recorder. The strain output is recorded on one axis of an x-y recorder and load is recorded on the other axis, providing a direct load-extension record. The extensometer is calibrated before and after each test on a standard 0.025-mm (0.0001-in.) calibrating fixture.

The question of validity of measurement was resolved in various ways. First, the extensometer was used to obtain the elastic modulus of hardened steel wire. This agreed within 3% with quoted values. Second, to check on extensometer averaging, several samples of an aluminum alloy were slightly bent before mounting the extensometer, and were pulled into the plastic range. The slope of the elastic line was quite sensitive to the amount of pre-bending of the specimen, and the elastic modulus was obtained only on unbent wires, indicating that averaging was not achieved. Tests performed on tungsten single crystals are considered valid when the elastic line produced by the extensometer is within a few percent of that calculated for the specimen. Figure 15 shows the load-extension diagram for crystal TH-5, the elastic line obtained from the diagram, and calculation of the elastic modulus. The calculated value, $E = 34.0 \times 10^3 \text{ kg/mm}^2$, compares well with the accepted value, $E = 36.0 \times 10^3 \text{ kg/mm}^2$. The proportional limit is defined for our purposes as the first deviation from a valid elastic line. There is obviously some uncertainty concerning the exact value, but since the strain sensitivity is held constant for all tests, it appears to be quite reliable as a comparative measure.

Figure 16 compares the stress-plastic-strain data obtained from several crystals grown at General Atomic with data recently obtained from East German work.⁽²⁵⁾ The proportional limits and work-hardening rates for TH-5 and TH-7 are quite similar to the East German data, although the helium temperature resistance ratio for their crystals is $\sim 100,000$. This ratio as measured by the eddy-current decay method for TH-7 was found to be $\sim 23,000$ (see Fig. 12). The data plotted for TH-14 show both a lower proportional limit and a lower work-hardening rate. Specimens for the first irradiation capsule were made from TH-14. Resistivity measurements will be made on the remaining portions of this crystal.

1.2.3. Evaluation of Source Materials

Two source materials were chosen for evaluation as starting materials, one obtained from Westinghouse Electric Corporation, the other from San Fernando Laboratories. Tungsten obtained from Westinghouse (courtesy

Fig. 14--Clip-on extensometer

of H. Sell) was in the form of ~ 2 -mm- diameter rod. This material was hot-swaged by Westinghouse from a larger diameter tungsten single crystal which had a stated residual resistivity ratio Γ (R_{2980K}/R_{40K}) of $\sim 30,000$. The interstitial impurity content c was estimated by scattering elections and using the relationship given by Seraphim,⁽¹⁶⁾ $c = 2.7 (1/\Gamma)$ (atom-%); this estimate yields a value for c of $\sim 9 \times 10^{-7}$ (atom-%). This value would appear to approach the purities required in the program; however, chemical analysis⁽²⁶⁾ has indicated a carbon content of 10 to 50 ppm (wt). It appears from this that, at least for the case of carbon, the resistance ratio per se is not meaningful. Load-extension curves constructed for two single crystals grown from the Westinghouse starting material are shown in Fig. 17. No extensometry was available at this time, and the extensions were obtained by cross-head displacement and post-test measurements. Noted on Fig. 17 for TW 2-1 is the stress at $\sim 2\%$ strain (124 kg/m^2).

At about the same time the Westinghouse material was purchased, bulk tungsten that was vapor-deposited from hexafluoride gas became available from San Fernando Laboratories. This material was reportedly

Fig. 15--Extension curve for TH-5

quite low in carbon, which is difficult to remove from tungsten, and it was primarily on this basis that vapor-deposited stock was chosen for the second source material. Specimens suitable for zone refining were prepared from a tube 25 cm in length with a 2-mm wall thickness. Figure 18 presents a load-extension diagram for an early crystal grown with the Mark I gun in the electron-beam zoner. The stress at 2% strain is indicated (115 kg/mm^2), but is not vastly different from the Westinghouse tungsten. A chemical analysis for the vapor-deposited material before and after one-pass zone refining is presented in Table 2. Within the accuracy of the measuring methods used, it can be seen that the carbon content is quite low. No resistivity ratio measurements were performed at this time; the choice to use vapor-deposited material, however, was made primarily on the basis of low initial carbon content.

Fig. 16--Room-temperature stress-strain curves for East German crystals and General Atomic crystals grown from vapor-deposited stock

Some qualitative indications of the purity of crystals grown from vapor-deposited material can be seen in Figs. 19a, b, and c. A vapor-deposited specimen was not melted completely through, which resulted in a small surface section of polycrystalline tungsten. This section was quite easily bent at room temperature, as seen in Fig. 19a. Figures 19b and c show a zoned tungsten single crystal that was successfully rolled to ~70% reduction of area at somewhat above room temperature.

Fig. 17--Room-temperature load-extension diagram for tungsten single crystals grown from Westinghouse material; orientation as shown

Fig. 18--Room-temperature load-extension diagram for tungsten single crystal grown from San Fernando Laboratories material; orientation as shown

Table 2
 IMPURITY ANALYSIS OF VAPOR-DEPOSITED TUNGSTEN
 BEFORE AND AFTER ZONE REFINING

Element	Content by Weight (ppm)	
	Starting Material	Zone Refined
H ₂	17	<1
O ₂	55	3
N ₂	24	<1
C	5-6	<3
Ag	N<0.5	N<0.5
Al	8	N<1
As	N<20	N<20
B	N<4	N<4
Ba	N<2	N<2
Be	N<1	N<1
Bi	N<1	N<1
Ca	N<10	N<10
Cd	N<8	N<8
Co	N<1	N<1
Fe	2	2
Hg	N<8	N<8
Mg	1	<0.5
Mn	N<1	1
Mo	N<200	N<200
Na	N<20	N<20
Nb	N<6	N<6
Ni	N<4	N<4
Sb	N<6	N<6
Si	<2	2
Sn	N<2	N<2
Te	N<200	N<200
Th	N<8	N<8
Ti	N<6	N<6
Tl	N<8	N<8
V	N<8	N<8
Zn	N<20	N<20
Zr	N<20	N<20

NOTE: N < x = not detected, and x = limits of detection.

(a)

(b)

(c)

Fig. 19--(a) Crystal grown from vapor-deposited stock, then bent at room temperature; (b) and (c) rolled tungsten single crystal

1.2.4. Tungsten Irradiation

A program objective is to irradiate material of highest possible purity. The proportional limit and work-hardening rate are felt to be indicators of purity. Crystal TH-14 was chosen for the first irradiation mainly because of these measured properties. Figure 16 shows the plastic stress-strain curve for this material, and the East German data are included for comparison. The single crystal was cut into 3-cm lengths, and a 1.3-cm-long gauge section was ground to a uniform diameter on each specimen. The as-ground crystals were then electropolished in a 2% NaOH solution. Removal of 0.025 to 0.05 mm from the surface was sufficient to obtain sharp Laue back-reflection photographs. Tantalum-free molybdenum end grips were machined to fit the crystal, and the grips were welded to the tungsten specimen using the same electron gun and traverse mechanism as for zone refining.

Subcapsules were designed and machined from a low-iron aluminum alloy (6063) (see Fig. 20). To avoid strains induced by differential coefficients of expansion of the tungsten, molybdenum, and aluminum, the subcapsules were designed so as to contact the specimen only in the gauge length, leaving the ends free. The subcapsule material was chosen on the basis that no high-activity isotopes of appreciable half-lives would be produced. The brass screws holding the subcapsules together have similar activation properties. The tantalum-free molybdenum has no undesirable isotopes after ~ 30 days, which is the least time anticipated between reactor shutdown and delivery to General Atomic. The tungsten is not expected to exhibit an undue hazard from radioactivity when handled without shields or manipulators. (27)

The outside subcapsule dimensions, $1 \text{ cm} \times 5.5 \text{ cm} \pm 0.0025 \text{ cm}$, were chosen so as to be directly interchangeable with standard Charpy V-notch specimens in the Naval Research Laboratory (NRL) irradiation capsules. The experience of NRL indicates that a temperature of 115°C (240°F) is not exceeded at any point in the $5 \text{ cm} \times 5 \text{ cm}$ cross section of the entire capsule. No temperature monitors were included, since aluminum has a low gamma heating rate and good thermal conductivity compared with tungsten, molybdenum, or iron (the major constituent of the Charpy specimens filling the remainder of the capsule). Iron and titanium monitor wires were placed in Capsule 1 and iron wires only were placed in Capsule 2 to provide independent methods of obtaining integrated neutron flux. Capsule 2 contained, in place of titanium monitor wires, a 1.5-cm section of tungsten single crystal for internal friction studies. Figure 21 shows the capsule components before assembly. The subcapsules were shipped to NRL on October 16, 1964, for placement in an irradiation capsule to be inserted into the Low Intensity Training Reactor (LITR) on November 15, 1964. The expected integrated fast-neutron flux is $\sim 3 \times 10^{19} \text{ nvt.}$ (28) After

SECTION A-A

Fig. 20--Tungsten irradiation specimen in aluminum subcapsule

Fig. 21--Irradiation specimens, flux monitors, and subcapsule

reactor shutdown and before receipt by General Atomic, the various radioactive constituents of the capsule are expected to have a total activity less than 60 mr/hr at 30 cm. Table 3 lists the weights and expected activities of the various constituents. No removable contamination is expected on the specimen. At the low activities anticipated, it is planned to test the specimens in the same manner as uncontaminated ones, with the precaution of radiation monitoring of the specimens during the tests and of the equipment after testing. Specimens from the present capsules will very likely receive the highest dose to be used in these studies.

Table 3
CALCULATED RESIDUAL ACTIVITY FOR SPECIMEN
COMPONENTS AND SUBCAPSULE COMPONENTS

Material		Expected Activity After Reactor Shutdown (mr/hr/30 cm)	
Before Irradiation	After Irradiation	4 Weeks	6 Weeks
Specimen			
W ¹⁸²	Ta ¹⁸²	3	2.5
Mo ⁹⁸	Mo ⁹⁹	18	<1
Mo ⁹⁵	Nb ⁹⁵	20	16
Subcapsule and Flux Monitor			
Cu	---	Negligible	Negligible
Zn ⁶⁴	Zn ⁶⁵	4	3
Fe ⁵⁸	Fe ⁵⁹	6	4
Ti	---	Negligible	Negligible

Experiments planned for these specimens include recovery of yield strength and resistivity with annealing. A problem exists in trying to perform recovery-type experiments on specimens which do not exhibit a yield point as such. It has been our experience with tantalum ($\Gamma \sim 1000$), and has also been true with tungsten, that the classic yield point disappears with increasing purity. This is also a characteristic of the tungsten crystals presently being grown at General Atomic. For this reason, some effort has been made to determine a usable strain parameter such that these recovery-type experiments could be performed on a single specimen. Figure 22 presents the stress-plastic strain relationship for crystal TH-10, and Fig. 23 presents the data in semilog form. Also included in Fig. 23 is a plot of the slope of the stress-log plastic strain curve, and a distinct break in this relationship is found at a plastic strain of $\sim 10^{-3}$. This

Fig. 22--Stress-strain curve for TH-10 at room temperature

Fig. 23--Stress-plastic strain curve and stress-log plastic strain curve for TH-10 at room temperature

behavior has also been observed for several other crystals. A detailed interpretation of this strain region may be available from the internal friction experiments presently in progress. However, a speculation concerning this strain is that it represents the region where significant dislocation multiplication occurs. If this is so, this type of measurement provides a measure of plastic strain which should not be exceeded in the recovery of mechanical properties of irradiated tungsten. The reason for this, of course, is that straining the irradiated specimen into a region where large numbers of dislocations are generated could complicate the annealing behavior of the irradiated sample.

REFERENCES

1. Trozera, T. A., J. L. White, and R. H. Chambers, "A Program of Basic Research on Mechanical Properties of Reactor Materials," Summary Report, October 1, 1962, through September 30, 1963, USAEC Report GA-4900, General Atomic Division of General Dynamics Corporation, 62 p.
2. Keh, A. S., and S. Weissman, "Deformation Substructure in Body-center-cubic Metals," in Electron Microscopy and Strength of Crystals, G. Thomas and J. Washburn, Eds., Interscience, New York, 1963, Chap. 5, p. 321.
3. Swann, P. R., "Dislocation Arrangements in Face-centered Cubic Metals and Alloys," *ibid.*, Chap. 3, p. 131.
4. Shoeck, G., private communication.
5. Lothe, J., "The Effect of Temperature on Dislocations with Condensed Impurity Atmospheres. Theory of Dislocation Motion and Dislocation Break-away," Acta Met. 10, 663 (1962).
6. Van Torne, L. I., and G. Thomas, "Yielding and Plastic Flow in Niobium," Acta Met. 11, 881 (1963) (Lawrence Radiation Laboratory Report UCRL-1015).
7. Walker, R. M., "Electron Induced Radiation Damage in Pure Metals," in Radiation Damage In Solids, D. Billington, Ed., Academic Press, New York, 1962, p. 594.
8. Damask, A. C., "Recent Progress in a Theory of Vacancy-Annealing in Metals," *ibid.*, p. 553.
9. Thompson, M. W., "Radiation Damage in Body Centered Metals," *ibid.*, p. 753.
10. Wagenbloot, H., and A. C. Damask, "Kinetics of Carbon Precipitation in Irradiated Iron," Phys. Chem. Solids 23, 221 (1962).

11. Pfann, W. G., Zone Melting, John Wiley and Sons, Inc., New York, 1958.
12. Schadler, H. W., and J. R. Low, Jr., "Low Temperature Brittleness of Refractory Metals," Final Report to Office of Naval Research, General Electric Company Report 62-GC-206, April, 1962.
13. Murray, G. T., S. Weinig, and I. Drangel, "The Relation Between Vacuum and Purity in Float-Zone Melting of Refractory Metals," presented at a meeting of the Vacuum Metallurgy Society of New York, June, 1964, 22 p.
14. Becker, J. A., E. J. Becker, and R. G. Brandes, "Reactions of Oxygen with Pure Tungsten and Tungsten Containing Carbon," J. Appl. Phys. 32, 411 (1961).
15. Seraphim, D. P., J. I. Budnick, and W. B. Itner III, "Single Crystal Growth and Purification of Tantalum," Trans. AIME 218, 527 (1960).
16. Seraphim, D. P., D. T. Nowick, and J. I. Budnick, "The Effects of Imperfections on the Superconducting Critical Temperature of Tantalum," Acta Met. 9, 446 (1961).
17. Verhoeven, J., "Electrotransport in Metals," Metals Rev. 8, 311 (1963).
18. DeBoer, J. H., and J. D. Fast, "Electrolysis of Solid Solutions of Oxygen in Metallic Zirconium," Réc. Trav. Chim. 59, 161 (1940).
19. Angus, J., D. V. Ragone, and E. E. Huckle, "The Effect of an Electric Field on the Segregation of Solute Atoms at a Freezing Interface," in Physical Chemistry of Process Metallurgy, Part 2, G. R. St. Pierre, Ed., Interscience, New York, 1959, p. 833.
20. Pfann, W. G., and R. S. Wagner, "Principles of Field Freezing," Trans. Met. Soc. AIME 224, 1139 (1962).
21. Hay, D. R., and E. Scala, "Electrodiffusion and Zone Refined Tungsten," Materials Science Center, Cornell University, Report No. 250, 1964, 28 p.
22. Olsen, J. L., Electron Transport in Metals, Interscience, New York, 1962.
23. Bean, C. P., et al., "Eddy-Current Method for Measuring the Resistivity of Metals," J. Appl. Phys. 30, 1976 (1959).
24. White, G. K., and S. B. Woods, "Electrical and Thermal Resistivity of Transition Elements at Low Temperature," Phil. Trans. Roy. Soc. London, Ser. A, 251, No. 995, 273-302 (1959).
25. Finke, Peter, et al., "Licht- und elektronenmikroskopische Beobachtung von Gleitlinien auf elektronenzonengereinigtem Wolfram," Sonderdruck aus Ausscheidungsverfahren in Legierungen, Akademie-Verlag, Berlin, 1964.

26. Schultz, H., "Die Erholung des Elektrischen Widerstandes von Kalt Verformten Wolfram," Acta. Met. 12, 649 (1964).
27. J. Moteff, private communication.
28. L. Steele, private communication.

II. DISLOCATION DYNAMICS

The new methods of study of the mechanical state of a metal (acoustical spectroscopy and amplitude-dependent modulus-defect measurements) have provided unique insight into the underlying mechanisms which control plastic deformation in the refractory bcc metals over ranges of purity, strain rate, stress, and temperature.

Through the acoustical study of very high purity Ta, it has been determined that the mobility of dislocations under low external stresses must be spatially very heterogeneous, resulting in some parts of the dislocation network being able to move rapidly in response to an applied stress while other parts remain frozen. These results are expressed by the existence of a number of very broad energy bands in the dislocation relaxation spectrum of a refractory bcc metal. The high-amplitude modulus-defect measurements have confirmed that these energy bands most probably correspond to various components of the dislocation network. These high-amplitude measurements have also shown that the various energy bands can have their energy lowered through the application of sufficient stress; and it is generally found that the stress coupling factor (or activation volume) of the highest energy process is larger than that of the lower energy processes.

As a result of these studies, a model of stress-assisted, thermally activated, dislocation motion has been developed and is now being investigated. The essential idea of this model is that long-range dislocation motion in these metals is dependent upon the slowest moving member of the heterogeneous dislocation network. The knowledge of the existence of many components in the network, each with its particular mobility and stress concentration factor, provided the original incentive for the construction of the multicomponent model of yield and flow.

It is felt that the methods of acoustical spectroscopy and high-amplitude modulus-defect measurements, developed over the years under the present contract and applied to the study of the mechanisms of yield and flow in the bcc refractory metals, have matured considerably during the last year. Thus, with the feeling of an enhanced perspective, the following summary review is concerned mainly with a critical evaluation of the models of dislocation motion evolved by the dislocation dynamics group not only in 1964 but over the past several years.

2.1. MODELS OF DISLOCATION RELAXATIONS IN BCC TRANSITION METALS

2.1.1. Dislocation Relaxation Versus Point-defect Relaxation

The defects that cause the mechanical relaxation peaks⁽¹⁾ must be closely associated with the dislocations that produced the plastic flow and/or the defects produced by the plastic flow; e. g., self-interstitials, vacancies, divacancies, dislocation dipoles, etc.

2.1.1.1. Instability of Regular Snoek Effect. Chambers and Schultz⁽²⁾ found that the α and β deformation-induced peaks are stable at temperatures immediately above their peak temperatures for low-frequency measurements (1 to 10 cps). They conclude that any explanation of these peaks which is based on a point-defect mechanism must require that the mean time of stay (mts) of the defect for reorientation be considerably smaller than the mts for the diffusion of the defect through the lattice. This conclusion was reached by examining the consequences of considering the relaxation peaks to be associated with the stress-induced jumping of point defects by a Snoek-type mechanism⁽³⁾ where the jumping time of the defects is assumed to be also nearly equal to the characteristic time for their migration through the lattice. The resulting damping peaks should be unstable at temperatures above the peak temperature. For stability above the peak temperature, it would be required that (a) the defects are in equilibrium concentration at these temperatures, or (b) their removal rate is not diffusion controlled, implying that the defects must move over a large potential barrier to be rendered ineffective. The equilibrium-concentration hypothesis is not reasonable because the peaks would then appear spontaneously; they would not require plastic deformation. The second alternative is not probable because most defect-removal (annealing) processes discussed in the current literature are diffusion controlled. The observed stability of the α and β damping peaks⁽²⁾ therefore led to the conclusion stated above that for any explanation based on a point-defect mechanism, the mts of the defect for reorientation is considerably smaller than the mts for diffusion.

A point defect with just such characteristics, which could lead to a stable Snoek-like effect, has been considered to exist in fcc metals; i. e., the split, or dumbbell, interstitial,^(4,5) In fcc Ni, the dumbbell interstitial is thought to have a relaxation energy, due to rotation about its center of mass, of 0.81 ev,⁽⁶⁾ and a diffusional energy, for mass transport, of 1.02 ev. Thus in Ni the difference in energy for the relaxation process (rotational jumping) and the mass-transfer process is about 0.2 ev. In bcc Nb, the α peak was found to have a relaxation energy not in excess of 0.3 ev, while the annealing process had a lower limit of 1 ev.⁽²⁾ Hence, in bcc Nb, the difference between the relaxation and annealing energy is 0.7 ev, or over three times that observed for Ni. Similarly, for bcc Mo,

the relaxation energy of the β peak is 0.5 eV with an annealing energy of 1.3 eV, yielding a difference of 0.8 eV.⁽¹⁾ From these results it is apparent that if one considers point defects introduced during plastic flow as the source of the damping peaks in the bcc transition metals, then these point defects must be endowed with the somewhat unlikely property of having a relaxation energy which is 0.7 eV less than their diffusion energy.

It is interesting to consider, in the light of these observations, the idea of constrained dislocations as the source of the relaxations. Chambers and Schultz⁽²⁾ conclude from their observations on Nb that the α peak behaves as if it is the result of relaxation of a mobile defect trapped in a relatively immobile structure. They identify the relatively immobile structure with the dislocation network, which is anchored by nodal intersections and point-defect pinning points. Between the pinning points, the dislocation is considered to be relatively free to move, possessing a temperature-dependent mobility. They consider the relaxing defect to be either (a) the free dislocation loop whose mobility is controlled by the generation rate of pairs of kinks,⁽⁷⁾ or (b) the free loop whose mobility is controlled by the motion of an atmosphere of point defects surrounding the loop.^(8, 9)

The introduction of the dislocation line as the active relaxation element thus easily disposes of the problem of the large separation between the relaxation and diffusion energies that would be needed if a Snoek-like effect were the relaxation process. Chambers and Schultz⁽²⁾ proposed that the energy for the annealing of these damping peaks is associated with the energy for diffusion of pinning defects to the dislocation line; the presence of pinning defects acts to reduce the dislocation loop length, which decreases the relaxation strength of the free loop relaxation process.

Further evidence against a Snoek-like point-defect relaxation comes from the temperature dependence of amplitude-dependent damping. Chambers⁽¹⁰⁾ has shown that the amplitude-dependent damping in deformed high-purity Ta increases with increasing temperature in several well-defined stages. The beginning of each stage corresponds to the temperature of the deformation-induced peaks measured in the amplitude-independent region at very low strain amplitudes of about 1×10^{-7} .

The amplitude-dependent measurements by Chambers also showed strong evidence of breakaway at amplitudes greater than 2×10^{-5} ; he therefore concluded that the amplitude dependence was due to a hysteresis-producing depinning of dislocations from pinning points. This component of the damping was identified as being due to the motion of dislocations, and was observed to be dependent on the temperature in the same way as was the low-amplitude (amplitude-independent) component of the damping. It was thus concluded that the low-amplitude component was also due to the motion of dislocations and not to point-like defects.

Further evidence comes from observation of a low-temperature deformation effect. DeBatist⁽¹¹⁾ claims that plastic deformation at liquid nitrogen temperature of "as received" Nb wire "partly suppresses" a group of damping peaks found near 220°K (0.5 cps). As a result of room-temperature annealing, the peaks partially recover. DeBatist argues that the relaxation of intrinsic point defects would not be expected to lead to these results, since one would not expect peaks due to this source to be suppressed during the movement of dislocations. He therefore considers that the damping peaks are associated with either or both of the possibilities discussed above. (2)

In summary, the most convincing arguments against the theory that the α or β peaks are due to a Snoek-type relaxation of point defects introduced by deformation are (a) that both of the peaks are stable at temperatures above the peak temperatures, and (b) that the temperature dependence of the amplitude-dependent damping components usually associated with the depinning of dislocations closely corresponds to the temperatures of the amplitude-independent peaks.

2.1.2. Model of Stress-amplitude and Temperature-dependent Dislocation Motion in bcc Transition Metals

The following is a treatment of a new model of stress-amplitude and temperature-dependent dislocation motion, which may be applicable to high-stress-amplitude damping and modulus measurements. This model represents a departure from the Koehler⁽¹²⁾-Granato-Lücke (KGL) model, the Rogers⁽¹³⁾ modification of their model, and the Swartz-Weertman⁽¹⁴⁾ model. The acoustical energy loss resulting from high-stress-amplitude dislocation motion depends, in the KGL model, on an irreversible breakaway of dislocations from pinning points during a portion of the first quarter of the stress cycle. According to the KGL model and the Rogers modification of this model, the breakaway occurs in a short time compared with the period of measurement. Thus, the resulting hysteresis is independent of frequency; i.e., the energy loss or internal friction at high amplitudes is classed as static hysteresis. (15)

The assumption in the present formulation of oscillating-stress-amplitude dependence is that all the damping processes are essentially reversible; i.e., given sufficient time, any obtainable configuration can exist. This is not true under the assumptions of the KGL model, which is constructed to be valid only at absolute zero temperatures, whereas the present model is based on thermal activation and, therefore, is automatically designed to work at standard temperatures.

A more recent formulation of the amplitude-dependent internal-friction problem by Friedel⁽¹⁶⁾ takes thermal activation into account, but

applies it only to unrestricted dislocation motion. Friedel's model is incorporated in the present model as a special case of the stiffness coefficient C being equal to zero--a case of particular importance at very high stresses, as will be shown later in this section. The following treatment of dislocation motion emphasizes two important characteristics found in the measurements of the damping and the modulus defect of the bcc transition metals: In the temperature and frequency range studied, the damping and modulus defect in these metals is (a) thermally activated and (b) stress-amplitude dependent, i. e., nonlinear.

The existence of a wide range of activation energies arranged in broad energy bands suggests that dislocations in these metals must move by a number of thermally activated rate processes with energy barriers distributed around certain central values. The nature of these energy barriers will be discussed in Section 2.1.3.

2.1.2.1. Diffusing Particle Representation of Dislocation Motion. Weertman⁽¹⁷⁾ represented the motion of a constrained dislocation line moving through a number of potential barriers at a finite temperature by the thermally activated motion of a representative particle in a multiwell potential, as shown in Fig. 24a. The multiwell potential is a superposition of a series of equally deep, periodically spaced potential wells and a smooth parabolic potential. The periodic potentials represent the short-range

Fig. 24--Multiwell potential representation of dislocation motion; (a) parabolic long-range potential; (b) constant long-range potential; (c) double-well potential

interaction of the dislocation line segment with local internal stresses associated with impurities, etc.; the gradient of the parabolic potential represents the restoring force developed by the segments interacting at long range with themselves (line tension) and other dislocations.

Weertman showed that the equation of motion of such a representative particle may be approximated by a simple linear equation:

$$\frac{1}{\mu} \dot{x} + Cx = \sigma b , \quad (1a)$$

or

$$\dot{x} = \mu b \sigma - \mu Cx , \quad (1b)$$

where μ = mobility,

C = stiffness coefficient,

σ = applied shear stress,

b = Burgers' vector, and

x = average displacement of the dislocation line normal to its axis in its slip plane.

A more general form of Eq. (1b) is

$$\dot{x} = \mu(\sigma, T) b \sigma - \mu(\sigma, T) C(x) x . \quad (1c)$$

Equation (1c) is identical to that of a driven, nonlinear, overdamped oscillator, i. e., of an oscillator whose viscous damping term greatly exceeds the inertial term. Such an overdamped oscillator will not oscillate when undriven; it relaxes toward its equilibrium position with no overshooting. Since there will be frequent occasion to refer to the overdamped oscillator, we will call it a "relaxator," in obvious reference to its essential characteristic, and Eq. (1c) the "relaxator equation."

Several important assumptions are made when the complex motions of a dislocation line are reduced to the relaxator equation. First, as Weertman initially stated, it is assumed that only the fundamental vibrational mode of the dislocation line contributes to the displacement of the line under thermal excitation. Thus, it is assumed that the cooperative motion of a line may be approximated by the motion of only the fundamental vibrational mode of the line. It is also assumed that this mode may be represented as a particle which diffuses according to the standard rate equations through a field of stress barriers. Second, as will be seen, an important restoring force is neglected in the above treatment because of the spatial gradient of the configurational entropy associated with the various dislocation vibrational modes.

In establishing Eq. (1a), it is assumed that the relation between the size of the individual well depth and spacing, and the curvature of the superimposed long-range potential is such that it is meaningful to separate out a mobility term and a stiffness term. In the extreme case for $C \rightarrow 0$, μ may be computed as follows: Consider a particle moving in a uniform periodic potential with well height H (see Fig. 24b); then the velocity $\dot{x}$ of the particle is given by

$$\dot{x} = \nu a \left\{ \exp \left[- \left(\frac{H - v\sigma}{kT} \right) \right] - \exp \left[- \left(\frac{H + v\sigma}{kT} \right) \right] \right\}, \quad (2a)$$

or

$$\dot{x} = 2\nu a \sinh \left(\frac{v\sigma}{kT} \right) \exp \left(- \frac{H}{kT} \right), \quad (2b)$$

where ν is the attempt frequency, a is the well separation, and v (or activation volume) is the rate at which H is decreased by an increasing stress, σ ; $v = \partial H / \partial \sigma$.

The first term of Eq. (2a) gives the rate of forward jumps, and the last term gives the rate of backward jumps. In the limit of $v\sigma/kT \ll 1$, Eq. (2b) becomes

$$\dot{x} = 2\nu a \exp \left(- \frac{H}{kT} \right) \cdot \frac{v\sigma}{kT}, \quad (3a)$$

or

$$\dot{x} = \mu(T) \sigma b, \quad (3b)$$

where

$$\mu(T) \equiv \frac{2\nu v a}{kT b} \exp \left(- \frac{H}{kT} \right). \quad (3c)$$

In the limit of the $v\sigma/kT \gg 1$, Eq. (2b) becomes

$$\dot{x} = \frac{\nu a \exp \left[- \left(\frac{H - v\sigma}{kT} \right) \right] \sigma}{\sigma}, \quad (4a)$$

or

$$\dot{x} = \mu(T, \sigma) \sigma b, \quad (4b)$$

where

$$\mu(T, \sigma) \equiv \frac{\nu a}{b} \cdot \frac{\exp \left[- \left(\frac{H - v\sigma}{kT} \right) \right]}{\sigma}. \quad (4c)$$

On the other hand, for a given well height H and well separation a , μ and C change as the curvature of the superimposed long-range potential becomes greater; for example, consider the extreme case of a double-well potential (see Fig. 24c):

Let the analog to the displacement x used above be given by

$$x = N_a - \frac{N}{2}, \quad (5)$$

where N_a is the density of particles in wells of type a and N is the density of particles in type a and b wells combined. Thus, if Γ_{ab} is the jumping rate of particles from a to b , and Γ_{ba} is the rate from b to a , then the flux of particles out of type- a wells is

$$-\dot{N}_a = (\Gamma_{ba} + \Gamma_{ab}) N_a - \Gamma_{ba} N, \quad (6)$$

or from Eq. (5),

$$\dot{x} = \frac{-(\Gamma_{ba} - \Gamma_{ab})N}{2} + (\Gamma_{ba} + \Gamma_{ab})x. \quad (7)$$

Comparing Eq. (7) with Eq. (1b),

$$-\Gamma_{ba} + \Gamma_{ab} = \frac{2b\mu\sigma}{N};$$

$$\Gamma_{ba} + \Gamma_{ab} = -\mu C;$$

or

$$\mu = \frac{N(-\Gamma_{ba} + \Gamma_{ab})}{2b\sigma},$$

and

$$C = \frac{2b\sigma}{N} \frac{(\Gamma_{ba} + \Gamma_{ab})}{(\Gamma_{ab} - \Gamma_{ba})}.$$

Thus, if

$$\Gamma_{ab} = \Gamma_0 \exp \left[- \left(\frac{H - v\sigma}{kT} \right) \right]$$

and

$$\Gamma_{ba} = \Gamma_0 \exp \left[- \left(\frac{H + v\sigma}{kT} \right) \right],$$

then

$$\mu = \frac{N \Gamma_o \sinh(v\sigma/kT) \exp(-(H/kT))}{b\sigma},$$

and

$$C = \frac{b\sigma}{N} \frac{\sinh(2v\sigma/kT)}{[\sinh(v\sigma/kT)]^2}.$$

Now, if $v\sigma/kT \ll 1$, then

$$\mu(T) = \frac{N \Gamma_o v}{b kT} \exp\left(-\frac{H}{kT}\right), \quad (8a)$$

and

$$C(T) = \frac{2b kT}{vN}. \quad (8b)$$

However, if $v\sigma/kT > 1$, then

$$\Gamma_{ab} \gg \Gamma_{ba};$$

and

$$\mu(\sigma, T) = N \Gamma_o \frac{\exp[-(H + v\sigma)/kT]}{2b\sigma}, \quad (9a)$$

and

$$C(\sigma) = \frac{2b\sigma}{N}. \quad (9b)$$

By comparing the expressions for μ and C for the two extreme kinds of relaxators considered above, several important features are evident:

- The stiffness coefficient for the first kind of relaxator is derivable from the spatial gradient of the long-range potential; if the potential is parabolic, C is independent of the displacement.
- The stiffness coefficient is an increasing function of stress in the high-stress limit of the double-well potential. This type of stress dependence is characteristic of a hard spring and will be referred to as characteristic of a restricted long-range potential. The implication of such a potential is, of course, that the displacement saturates with increasing stress.
- The stiffness coefficient in the case of the symmetrical double-well potential at low stresses arises from a different physical origin than in the first case. In the absence of an external stress,

a particle placed initially in either well a or well b experiences a "restoring force" that tends to distribute it equally, on a time-average, in both well a and well b. The origin of this restoring force is the spatial gradient of the entropy of the system. The entropy of the system is increased if the particle does not remain in well a but is distributed between both wells.

The case of the symmetrical double-well potential illustrates (at low stresses, for which $v\sigma < kT$) a pure case in which the restoring force, and hence the stiffness coefficient C , is determined by the gradient of entropy; whereas the first type of potential at high stresses illustrates a pure case in which C is determined by the gradient of the potential energy of the system.

At very low stresses, even in the case of the first type of potential, the stiffness coefficient C will depend largely on changes in the entropy of the line segment with displacement because the atomic discreteness of the wells permits the dislocation to occupy only the several wells on either side of its equilibrium position. For such small displacements, the wells are only slightly influenced by the superimposed long-range potential and must obtain most of their restoring force from entropy changes.

We have seen that the symmetrical double-well potential yields a stiffness coefficient that is proportional to temperature T and inversely proportional to the activation volume v . Therefore one may expect that in the general case of a series of periodic potential wells with a smoothly increasing symmetrical superimposed potential, C may be expressed as

$$C(\sigma, T) = C_1 + C_2, \quad (10)$$

where

$$C_1 = C_1(x), \quad \text{and} \quad C_2 \propto kT/v; \quad (11a)$$

for small x ,

$$C_1 \rightarrow 0, \quad \text{and} \quad C \propto kT/v. \quad (11b)$$

C_1 is obtained from the gradient of the long-range potential and C_2 is determined by contribution from entropy. It is expected that for a certain range of stresses, C_1 should be larger than C_2 , whereas for very small displacements from equilibrium, C_2 will increase in relative size.

From Eqs. (3c), (4c), (8a), and (9a), it can be seen that the mobility μ retains the same dependence on σ and T in both extreme cases of a superimposed long-range potential; i. e., it is independent of σ for small stresses ($v\sigma < kT$) and strongly dependent on T (through the Boltzmann

relation). On the other hand, at high stresses ($v\sigma > kT$), μ is stress-dependent as well as temperature-dependent through the activation-volume term $v\sigma$.

In the general case of a superimposed long-range potential, the effect of the application of a stress on μ , in the stress range $v\sigma > kT$, is difficult to estimate. A more detailed treatment of the balance in rate processes between the various potential wells is required. In a first approximation, it appears that the application of an external stress leaves unchanged the relative heights of the barriers between the various wells, changing only the equilibrium position; i. e., although the stress increases the rate of forward jumps, the rate of backward jumps also increases. Thus, the activation volume v appears to be small in such a case, (18) becoming larger as the stress σ increases and satisfies the condition $v\sigma > kT$.

If both μ and C are independent of σ and x , the relaxator equation, Eq. (1c), is identical with the equation for the standard linear solid. In Section 2.1.2.2 we discuss the behavior of the internal friction and modulus defect associated with the dynamic solutions to the standard linear solid equation as C and μ become dependent upon x and σ , i. e., as a departure is made from linearity.

2.1.2.2. Nonlinear Damping and Modulus Defect. Equation (1c) will first be expressed in terms of measurable quantities. The amount of strain ϵ_d produced by a length Λ (in cm/cm³) of dislocation moving an average distance x is given by

$$\epsilon_d = \alpha \Lambda b x, \quad (12)$$

where α is an orientation constant. From Eq. (12), Eq. (1a) becomes

$$\frac{\partial \epsilon_d}{\partial t} + C \mu \epsilon_d = \alpha \sigma \Lambda b^2 \mu + \alpha \frac{\partial \Lambda}{\partial t} x b. \quad (13)$$

If the experimental conditions are arranged so that the second term of Eq. (13) is small compared with the first term, then Eq. (13) may be expressed as

$$\frac{\partial \epsilon_d}{\partial t} = -\mu C \left(\epsilon_d - \frac{\alpha \Lambda b^2}{C} \sigma \right). \quad (14)$$

Thus, the relaxation time τ and the relaxation strength Δ_m are given by

$$\tau = \frac{1}{\mu C}, \quad (15)$$

and

$$\Delta_m = \frac{\alpha \Lambda b^2 G}{C}, \quad (16)$$

where $\sigma = G\epsilon$, G being the unrelaxed shear modulus and ϵ the elastic strain. For dynamic experiments, i. e., $\sigma = \sigma_0 e^{i\omega t}$ with ω the angular frequency, the internal friction (if $< 10^{-1}$) can be expressed as a phase angle, $\phi (=Q^{-1})$. Thus,

$$\phi = \Delta_m \frac{1}{(\omega\tau)^{-1} + \omega\tau}, \quad (17)$$

and the modulus defect

$$\frac{\Delta M}{M} = \frac{M' - M}{M}, \quad (18)$$

$$\frac{\Delta M}{M} = \Delta_m \frac{1}{1 + (\omega\tau)^2}. \quad (19)$$

The internal friction is a maximum ϕ_m when $\omega\tau = 1$ or when $\omega = \omega_p$, with $\omega_p = \mu C$; then

$$\phi = \frac{\Delta_m}{2} = \frac{\alpha \Lambda b^2 G}{2C}; \quad (20)$$

and therefore $\Delta M/M$ at the internal-friction peak is

$$\left(\frac{\Delta M}{M}\right)_P = \frac{\Delta_m}{2}. \quad (21)$$

For comparison with experiment, it is useful to express both ϕ and $\Delta M/M$ in terms of temperature, or more conveniently, as a function of $1/T$. In Fig. 25 both the internal friction and the modulus defect, expressed in units of $(\alpha \Lambda b^2 G)/2$, are plotted as a function of H/kT for values of C .

Figure 25 shows that as C decreases, both the internal friction peak and the modulus-defect inflection point move to slightly higher temperatures and the peak and the defect increase their strength. Figure 25 also shows that increasing μ will shift the peak in the internal friction and the inflection point in the modulus defect toward lower temperatures.

The implications of these observations will now be examined in terms of the type of behavior that can be expected of the internal friction and modulus defect from this model as the oscillating stress amplitude is increased.

Fig. 25--Damping and modulus defect versus $1/T$ curves, showing effect of magnitude of stiffness coefficient C

First, let us examine the stress-amplitude dependence of Q^{-1} to be expected from a restricted type of potential such as the Snoek-effect, double-well potential (see Fig. 26a). A Q^{-1} versus T curve for increasing oscillating σ is shown in Fig. 26b. For small σ , Q^{-1} is independent of σ ; as σ increases, so that $v\sigma \sim kT$, the peak should slowly shift to lower temperatures and decrease in height from the stress dependence of μ and C shown in Eqs. (9a) and (9b).

A modified restricted potential which produces more complicated stress-amplitude dependence is shown in Fig. 27a. For small stresses, Q^{-1} is independent of σ . As σ increases, the Q^{-1} peak should lose its $1/T$ relaxation strength dependence. At still higher stresses, it should begin to rise in strength as the average stiffness coefficient starts to decrease, since the middle part of the potential is a soft-spring type of potential. As σ increases still further, the relaxation strength saturates and begins to drop. The stress at which saturation in the peak height begins depends on the detailed form of the potential. Also, as the condition $v\sigma > kT$ is fulfilled, the peak begins to shift to lower temperatures (see Fig. 27b).

A simple, unrestricted periodic series potential is shown in Fig. 28a. For this type potential, $C = 0$, and thus no peak exists at finite temperatures. In Fig. 28b the Q^{-1} versus T curves for increasing σ are shown. The principal effect is the shifting of the Q^{-1} curves to lower temperatures as the mobility is increased by the stress-assisted process, as $v\sigma > kT$.

A superposition of two sinusoidal-type potentials is shown in Fig. 29a. The short-wavelength potentials of height H_1 represent local interactions, and the gradients of the long-wavelength potential of average height H_2 represent long-range internal stress fields from other dislocations, etc. At low stresses, in addition to the internal friction peak associated with the short wavelength potentials, there exists another peak, generally at higher temperatures and associated with the long-range potential barriers (see Fig. 29b). Of course, as the long-range potential-restricting boundaries recede to greater distances, this high-temperature peak moves to infinite temperature, as in the case of the unrestricted potential.

As the stress is increased, the low-temperature peak should behave like a peak associated with a soft-spring type of potential; i. e., it should increase in strength with increasing oscillating stress. At still higher stresses, several possibilities exist, depending on the relative sizes of the activation volumes v_1 and v_2 that correspond to each of the two peaks with energies of H_1 and H_2 . If v_1 is larger than v_2 , then as the stress is increased the high-temperature peak will shift to lower temperatures faster⁽¹⁹⁾ than will the low-temperature peak, resulting in an enhanced amount of relaxation on the high-temperature side of the low-temperature peak.

(a)

(a)

(b)

Fig. 26--(a) Double-well potential; (b) damping versus temperature for double-well potential, showing effect of increasing oscillating stress σ

(b)

Fig. 27--(a) Multiwell potential for a restricted, soft-spring-type, long-range potential; (b) damping versus temperature for this type of potential, showing effect of increasing σ

(a)

(b)

Fig. 28--(a) Multiwell potential for unrestricted long-range potential; (b) damping versus temperature for this type of potential, showing effect of increasing σ

(a)

(b)

Fig. 29--(a) Multiwell potential representing long-range internal stresses; H_1 is energy barrier associated with short-range potentials, H_i is energy barrier associated with long-range internal stress; (b) damping versus temperature for this type of potential, showing effect of increasing σ

It is important to note that in this example both relaxation processes are series-coupled, so that as the stress is increased, the high-temperature peak cannot move to temperatures below the low-temperature peak. Thus, any further shifting of the peaks by the application of higher oscillating stress is determined by the size of the activation volume of the low-temperature peaks.

Thus, as long as the applied stress σ_a is smaller than σ_i (σ_i will be roughly independent of frequency or temperature if the activation volume v_i is much larger than v_l ; furthermore, $\sigma_i = H_l/v_i$), the dislocation segments will be restricted to movement within only one of the large wells, with a mobility determined by the small well height H_l and a stiffness coefficient dependent on the stress amplitude and the curvature of the large well. As σ_a approaches σ_i , the dislocation ceases to be "trapped" by the large well. When $\sigma_a > \sigma_i$, the dislocation is freed from the well, and its motion is determined only by the stress-dependent mobility. This transition from motion restricted to the well to motion relatively unrestricted represents the transition from short-range dislocation motion in the amplitude-dependent internal-friction range to long-range dislocation motion representative of the beginning stages of plastic flow. Figure 30 shows four curves of internal friction versus temperature (infrasonic acoustical absorption spectra) for annealed high-purity Ta with a resistance ratio of ~ 1850 . These measurements were made at ~ 16 cps and at the following oscillating stress amplitudes: $1 \times 10^{-5}G$, $1 \times 10^{-4}G$, $4 \times 10^{-4}G$, and $9 \times 10^{-4}G$.

At the relatively low stress amplitude of $1 \times 10^{-5}G$, several peaks can be seen--the α band near $140^\circ K$, the β_1 peak near $200^\circ K$, and the β_2 band near $300^\circ K$. As the oscillating stress increases, the α band increases in strength, goes through a maximum near $4 \times 10^{-4}G$, and then decreases with further stress. Also, a slight shift to lower temperatures can be seen in the α band at high-stress measurements.

Perhaps the most remarkable effect of the increasing stress is a strong increase in internal friction in the β -band range: From a stress of $4 \times 10^{-4}G$ to $9 \times 10^{-4}G$, the large rise in internal friction shifts from above $300^\circ K$ to below $220^\circ K$.

From the proposed model, the rise and subsequent fall of the relaxation strength of the α band seems to fit qualitatively the behavior of a representative dislocation particle moving in a potential well as shown in Fig. 27. On the other hand, the combined behavior of the α band and the β band resembles, in several respects, the behavior of particles moving in a potential similar to that shown in Fig. 29. From the strong shift in the internal friction rise near the β -band region, an activation volume of $\sim 40 b^3$ has been determined, whereas the small shift shown by the α band at the

Fig. 30--Damping spectrum in high-purity Ta for 16 cps and various oscillating-stress spectrum

highest amplitudes suggests that the activation volume of this process may be small ($<10 b^3$).

2. 1. 2. 3. Three-well Potential Model Applied to Aging. The above formulation of dislocation relaxation may be considered to represent a continuum treatment whereby the effect of a superimposed potential on a series of potential wells is replaced by an effective-stiffness coefficient and the short-range potentials manifest themselves in a mobility term.

The important intermediate cases wherein the change of potential from well to well is not small or the number of wells is not large can only be represented by a detailed rate process treatment, even for small applied stresses. Mason(20) has considered the relaxation equation which results from such a detailed treatment of the three well potential, shown in Fig. 31. The central well is separated from the side wells by a potential barrier of height H . The potential base of the two side wells is A above the bottom of the central well. Thus the potential barrier seen by a particle in either of the side wells is $H-A$ for a jump in the direction of the central well and infinite in any other direction. Mason has shown that the relaxation strength of a relaxator with such a potential diagram is approximately proportional to $e^{+(H-A)/kT}$. Thus the height of the base of the side wells A plays an important role in determining the relaxation parameters of the three-well-potential relaxator.

Fig. 31--Three-well potential representation of aging;
energy A increases with impurity concentration

If it is assumed that the origin of the potential barrier H is some kind of short-range interaction of the dislocation segment with either the lattice or impurities randomly distributed off of the glide plane, then the parameter A is a measure of the increase in potential energy of the segment as it is displaced a lattice dimension. Calculation of A should be made using kink language (see Section 2.1.3.1), since such small displacements are involved; however, an estimate of the dependence of A on pinning-point concentration may be made for fairly high concentrations by assuming that the line tension of the segment supplies a restoring stress that depends on the separation between pinning points; thus

$$A = \frac{Gb^3}{4} \times \frac{b}{\ell} = \frac{Gb^3}{4} \times C, \quad (22)$$

where ℓ is the average distance between pinning points and C is the linear concentration of pinning points. Notice that the interpretation of H and A given above differs from that of Mason. It is assumed here that H is independent of ℓ and A depends on ℓ , whereas in Mason's treatment, A was independent of ℓ and H depended on ℓ .

From Eq. (22), it follows that the relaxation strength Δ will depend linearly on C :

$$\Delta \propto e^{-A/kT} = 1 - \frac{A}{kT} = 1 - \frac{Gb^3 C}{4kT}, \quad \text{if } \frac{A}{kT} \ll 1. \quad (23)$$

In addition, the relaxation time τ will also depend on C through the relation:

$$\tau = \tau_0 \exp \left[\frac{H - (Gb^3 C/4)}{kT} \right].$$

But since $\omega\tau = 1$ and $\omega = \text{constant}$,

$$H - \frac{Gb^3 C}{4} \propto kT_p. \quad (24)$$

Thus, in this model both the internal friction peak temperature T_p as well as the peak height Δ should decrease linearly with increasing pinning-point concentration, such as that occurring during an anneal.

2.1.3. Mechanisms Which Determine Mobility of Dislocations

As was seen above, the mobility μ may be expressed in terms of a thermally activated diffusion-like process in which elements of dislocations are considered to behave like simple atomic species receiving thermal assists over potential barriers of height H . Donth⁽²¹⁾ and Seeger, et al.; ⁽⁷⁾

treated one aspect of this general dislocation problem more rigorously without resorting to this questionable but simplifying atomic diffusion analog. Fortunately, the diffusion analog seems to represent the essential physical mechanism involved in thermally assisted dislocation motion. In the following description of the various proposed models for thermally activated dislocation motion, it should not be forgotten that most of the models are founded on this simple atomic diffusion analog.

The models can be divided into three classes according to the nature of the mechanism which determines the mobility of the dislocation segment.

- a. Intrinsic lattice mechanisms, in which the energy necessary to move the dislocation configuration will depend, in a periodic manner, on the details of the local atomic rearrangements necessary to accommodate the passage of the configuration. Since local shearing displacements are involved in this process, materials which resist shearing atomic displacements, i. e., have strongly directed bonds, can be expected to manifest the largest energy barriers to the motion of dislocation segments. The elementary jumping of geometrical kinks and the generation of the double kinks over the Peierls potential barrier determines the mobility in this class of intrinsic mechanism.
- b. Static (or fixed) point defects which act as a barrier to dislocation motion and hence determine the dislocation mobility. The elastic strain field surrounding a point defect fixed in the lattice can provide a substantial energy barrier to the motion of a dislocation. (22) In some materials, other types of interaction best described as electrical can be important (in addition to the elastic interaction) in determining the size of this kind of barrier.
- c. Mobile point defects, which, interacting with dislocation segments, can determine the mobility of the segment. If a sufficiently large force is acting between the dislocation and the point defects, so that moving the point defects along with the dislocation becomes energetically easier than freeing the dislocation from the defects, the activation potential for dislocation movement can be considered to be closely related to the diffusion energy of the defects in the combined strain field of the dislocation and the lattice.

2.1.3.1. Intrinsic Lattice Mechanism

Barriers to Kink Motion. The most elementary dislocation segment or element is the free or single kink, (23) which is a dislocation segment that connects two straight dislocation lines lying on a common slip plane but separated by a potential ridge between them. The potential ridge separating the two straight dislocations is referred to as the Peierls

potential. As slip progresses, the kink moving along the potential ridge results in the straight segments of the dislocation moving perpendicular to themselves. The kink should, in general, encounter a periodic potential barrier as it moves along the ridge;⁽⁷⁾ the size of this potential barrier is at present very difficult to estimate, but it is thought to be quite small in fcc metals and may be large in directed bond crystals like silicon; it may not be insignificant in some of the refractory bcc metals. Lothe and Hirth⁽²⁴⁾ and Lothe⁽²⁵⁾ point out that because of the small dimensions of a kink, its motion should thus be thought of as diffusing along the potential ridge, even in the absence of any kink potential barriers. Brailsford⁽²⁶⁾ hypothesizes that the kinks are abrupt, i. e., only one atomic distance wide and noninteracting; he assumes that there is a moderately substantial energy barrier over which they must jump. An important consequence of this extreme formulation of kink motion is that all dislocation motion under even relatively large stresses will cease at 0°K; i. e., the modulus defect would be zero until the temperature was increased to where the kinks could traverse the nonzero potential barrier at a rate determined by the measuring frequency. Also, since all kinks in this model require thermal activation for motion, the effective activation volume will be very small ($\sim 1 \text{ barn}^3$) and thus application of very high stresses will be required to provide effective stress-assisted motion at very low temperatures.

Seeger and Schiller⁽²⁷⁾ introduced interaction between kinks in the form of a coulombic elastic interaction potential. Southgate and Attard⁽²⁸⁾ combine the nonzero kink energy barrier of Brailsford with the kink-kink interaction of Seeger and Schiller and show that when the kink density is moderately high, a dislocation composed of kinks all of one sign behaves much like the usual string model of Koehler and Granato-Lücke, with a strongly temperature-dependent damping term depending exponentially on the size of the kink barrier H .

Coupled Kink Motion. The above mentioned treatments of elementary kink motion all assume that individual kinks interact with thermal waves, and individual kinks make jumps over potential barriers, whereas Mason⁽²⁹⁾ discusses the implications of coupled kink motion.

If these coupled kinks or "super-kinks" are stable, then the activation energy for their coupled motion will be proportional to their length, leading to a wide spectrum of activation energies. According to Mason, this spectrum could account for much of the relatively frequency-insensitive damping seen in many high-purity specimens; such a frequency insensitivity would then not be distinguishable from an amplitude-independent static hysteresis damping mechanism.

Nucleation and Growth of Kink Pairs. A straight dislocation parallel to the Peierls ridge must nucleate and expand a pair of kinks in order to pass over the Peierls potential barrier. Seeger⁽³⁰⁾ and Seeger, et al.,⁽⁷⁾ have extensively examined the statistical mechanics associated with this type of dislocation motion.⁽²³⁾

Conservative Jog Motion. If the dislocation lies on several slip planes, the jogs connecting the dislocations in the different planes may encounter a periodic lattice potential barrier that must be surmounted before conservative motion is possible. Hirsch⁽³¹⁾ has inferred the existence of such barriers on the basis of the behavior of much larger jogs (super-jogs) frequently observed in electron microscopy. If the energy barriers inhibiting kink motion are smaller than those inhibiting jog motion, then the application of stress can pile kinks up behind a jog and help lower the energy of the barrier over which the jog must jump. In this example, the existence of both kink-kink interaction and free-kink motion leads to a relatively large activation volume for stress-assisted thermal activation of the conservative jog. Feltham⁽³²⁾ has discussed the possibility that thermally activated conservative jog motion is responsible for the Bordoni peak in fcc metals.

Nonconservative Jog Motion. Schoeck⁽³³⁾ has proposed that the non-conservative motion of jogs may be the rate-controlling process for dislocation motion in bcc metals. Such motion requires the production of point defects, and thus the energy barrier is closely connected with the energy of formation of point defects in the vicinity of a dislocation.

2. 1. 3. 2. Static Point Defects

String Models. In most of the intrinsic barriers mentioned above, the potential energy is "polystable," i. e., a number of nearly equal potential energy positions are made possible by a small translation of the dislocation. The intrinsic barriers thus provide a "fine-grained" corrugated energy surface over which dislocation segments must move. Such an energy surface will allow the motion of the dislocation to be treated in the manner discussed in Section 2. 1. 2, where forward and backward thermally activated jumps of dislocation segments are almost equally likely under small applied stresses. It will be recalled that under these conditions the average velocity of the dislocation is proportional to the applied stress acting on the dislocation, thus allowing the motion of the dislocation to be treated as if it were moving in a viscous medium whose viscosity is characterized by an activation energy H and a temperature T .

If the energy barriers are not polystable, the resulting retarding forces are not generally expressible in such a simple fashion and thus would not be expected to give rise to linear relaxation effects. An

important example of a fixed-point-defect-type barrier which, in the absence of intrinsic barriers, will not give relaxation effects is the Koehler-Granato-Lücke pinned dislocation string model, in which exist isolated point defects with attractive potentials. In this model, the dislocation has a unique low-energy configuration at low stresses; only at high stresses do other positions of the dislocation become energetically favorable. Thus, the isolated fixed-point-defect barrier with an attractive potential will give relaxation effects at low stresses only when the pinned dislocation is under a constant stress bias, which serves to introduce bistable or polystable states. On the other hand, if the point defects exist as a random distribution of positive and negative strain centers, then polystable positions are available at low stresses. This kind of fixed-point-defect barrier has been used, together with a string model, for dislocation damping at high temperature by Weertman.⁽¹⁷⁾

It is interesting to note that in contrast to the case of isolated fixed attractive potentials, isolated fixed repulsive potentials should produce relaxation effects at low stresses. Another interesting variation using the string model of the dislocation is Bruner's⁽³⁴⁾ disassociated dislocation interacting with an attractive point-defect potential. This model is bistable for certain orientations of the total dislocation.

One of the most serious objections to any string model of relaxation effects, i. e., any model which neglects the Peierls lattice potential, is that many of the relaxation peaks have been measured using stress amplitudes which correspond to elastic strains of $\sim 1 \times 10^{-8}$ or less, which in many cases implies that the average displacement of a dislocation is considerably less than an atomic distance. This is particularly serious for a fixed-point-defect-barrier model of relaxation effects, since in some cases the average distance between fixed point defects is probably not less than 30 atomic distances.

Kink Models. If the interaction of a dislocation with the lattice is taken into account, an arbitrarily curved dislocation contains a certain kink density. When this kink density is low, a very small displacement of a dislocation parallel to itself is accomplished by the movement of the few kinks over considerable distance. Thus, if a static-point-defect barrier is assumed, the kinks can diffuse between the widely spaced point defects creating the relaxation. Hasiguti⁽³⁵⁾ has proposed such a model to explain the damping peaks found above the Bordoni peaks in fcc metals. Hasiguti neglects kink-kink interactions and assumes that the kinks diffuse along the dislocations in the manner considered by Lothe and Hirth.⁽²⁴⁾ Hasiguti also assumes that the point-defect interaction is repulsive and considers that the activation energy measured is the repulsive interaction energy of the point defect with the kink. With very low kink density, the restoring force for the relaxation process will be the configurational entropy,

as was seen in Section 2.1.2.2. For other orientations of the dislocation, the kink density will increase and the kink-kink interactions will determine the restoring force; also, the stress acting on a kink attempting to penetrate the point-defect barrier will increase, owing to the increased stresses from the kinks piled up behind it. This kink-kink interaction should lead to an increase in the activation volume for stress-assisted relaxation.

2.1.3.3. Mobile Point Defects

If the interaction between the dislocation and the point defects is strong enough, the dislocation will drag the point defects along with it, limited by the rate at which the defects can diffuse and by the restoring force acting on the dislocation. Once again, either the string or kink model may be considered to describe the behavior of the dislocation.

String Model. Cottrell and Jaswon⁽³⁶⁾ considered the dragging effect of a dilute atmosphere of impurities on the motion of a dislocation string. Kessler⁽⁹⁾ considered the effect of a cloud of vacancies on the mobility of dislocations in germanium. Schoeck⁽³⁷⁾ has considered the stress-induced ordering of a Snoek atmosphere of interstitial impurities surrounding a string-like dislocation in bcc metal, in an attempt to explain the Koester (cold-working) peak.

Kink Model. Okuda and Hasiguti⁽³⁸⁾ think of the mobile-point-defect barrier as consisting of a two-step process: (a) a double kink is nucleated by breaking away from a point defect, and (b) the point defect later diffuses after the double kink and pins it down.

2.1.3.4. Dislocation Lines

Gilman⁽³⁹⁾ proposed the dislocation dipole as a dislocation relaxator, to explain the Bordoni peaks. He points out that two closely spaced edge-dislocations of opposite sign, resulting from a dislocation cross-slip reaction, are bistable and thus should produce a relaxation. The activation energy barrier appears to be due to the elastic interaction of the two parallel dislocations and does not involve any intrinsic lattice interactions. However, the energy does depend on just how the dipole flips into its alternative position. If it is assumed that it starts out in a twisted two-state position, then the energy for moving the twist down the dipole is negligible unless it is assumed that there is an additional point-defect barrier to cross. The stability of closely spaced edge dislocations is questionable, since they are equivalent to a line of vacancies or interstitials.

2.2. DISCUSSION OF EXPERIMENTAL RESULTS AND MODELS OF DISLOCATION RELAXATIONS IN BCC TRANSITION METALS

In Section 2.1.1, evidence was presented which suggests that the damping peaks and associated modulus defects found at low oscillating-stress amplitudes in plastically deformed bcc transition metals arise from a type of defect which possesses the following properties:

- a. The time constant associated with its annihilation as an active relaxator (as in the aging experiments) is very long compared with its mean time of stay. This property is foreign to most of the point-type defects.
- b. The close correlation between the temperature of the amplitude-independent damping peaks and the temperature of the changes in amplitude-dependent damping suggests that there is a connection between the two phenomena. Since nonlinear stress-amplitude dependence is to be expected from the mechanics of constrained dislocation motion, whereas only linear behavior is expected of point-defect motion in realizable stress regions, the above mentioned correlation suggests that the amplitude-independent damping and modulus defects are associated with dislocation relaxations.

Observation (a) is consistent with the conclusion reached in (b), and therefore the dislocation relaxator is probably responsible for most of the damping and modulus-defect phenomena in the frequency and temperature ranges investigated for the refractory bcc transition metals.

2.2.1. Dislocation Relaxation Activation Energy Spectrum

It has been shown^(40, 1) that two of the most prominent peaks, α and β , in the temperature versus damping curves of deformed Ta, Nb, Mo, and W obey an Arrhenius relation, even though neither of the peaks represents a simple relaxation process with a single relaxation time. In fact, in Ref. 1 it is shown that a distribution in both energy and pre-exponentials is generally necessary to explain the peak shapes; it is thus perhaps more appropriate to refer to the peak energy as the peak-energy band. As the entire temperature range from 4.2°K up to 500°K is studied more carefully, it becomes apparent that many more energy bands exist, each seemingly associated with some special mode of motion of the dislocation network. At present, in addition to the more carefully studied α and β energy bands, there appears to be an α' band and an α'' band⁽⁴¹⁾ in deformed Nb, with energies lower than that of the α band. Little is known about either at present except that the α'' band is extremely wide in comparison with the α band.

There is evidence of a γ band of energies lying above the β energies. Most of the measurements on the energies and pre-exponentials of this process have been made at high oscillating-stress amplitudes⁽⁴²⁾ and give values of $E_\gamma > 0.9$ ev and $\log f_\gamma \sim 9$.

A detailed study of Nb⁽⁴²⁾ has recently shown at least three damping peaks which responded quickly to aging treatment in the 400°K temperature range. These three peaks have been labeled β_1 , β_2 , and β_3 , in order of increasing temperature. Little is known at present concerning the values of E_{β_1} , E_{β_3} and f_{β_1} , f_{β_3} ; however, the β_2 peak temperature seems to be consistent with the earlier measurements of the β peak in Nb.⁽¹⁾

From the above, it is evident that the dislocation relaxation activation spectrum in the most carefully studied bcc metals, Ta and Nb, is indeed complex. More than seven broad energy bands exist with energies starting with hundredths of electron volts in the α'' band and extending up to at least 1 ev in the γ band range. Unfortunately, many of these processes are so broad that very large frequency shifts must be employed to measure them adequately.

2.2.2. Conditions Necessary for Observation of Dislocation Relaxations

Well-annealed specimens of high-purity Ta, subject only to mounting stresses, show rather well-defined damping peaks and their associated modulus defects.⁽⁴²⁾ Furthermore, these peaks are enhanced by the application of increasing oscillating stress. Thus, gross deformation is not an essential condition for the observation of dislocation relaxations as long as the observations are made at sufficiently high oscillating-stress amplitude. The effectiveness of high oscillating-stress amplitude in increasing the relaxation strength of the damping peaks is particularly evident in cases of specimens which have been sufficiently aged in situ to eliminate the peaks for measurements made at low stress amplitudes ($< 10^{-6}$ G).

From these observations it appears that the total modulus defect of a specimen measured at sufficiently high oscillating-stress amplitude is relatively independent of the state of deformation in the range of small deformations, including the well-annealed and aged condition.

This result follows from the assumption that at high amplitudes the only constraints acting upon the dislocations are those due to dislocation-dislocation interaction, i. e., from nodal interactions of the dislocation network. The consequence of this is that the resulting modulus defect is expressible by the Friedel relation; i. e., the dislocation displacement is governed by the stretched-string model, which leads to

$$\frac{\Delta M}{M} = \alpha \Lambda L_N^2, \quad \text{where } \alpha \sim 5 \times 10^{-2}, \quad (25)$$

with Λ the total active dislocation density and L_N the average nodal network length. For dislocation networks of generally cubic structure, $\Lambda L_N^2 \sim 1$; whereas for networks with dense walls, $\Lambda L_N^2 \ll 1$; and for networks with looser construction than cubic, $\Lambda L_N^2 \gg 1$.

Thus, if the structure parameter ΛL_N^2 remains relatively unchanged from the annealed to a slightly deformed specimen, the high stress-amplitude measurements should not show significant changes in the total modulus defect (i. e., the modulus defect as measured at a temperature above all the relaxations). This lack of change would then result in the observed lack of sensitivity of the peaks to deformation for low amounts of deformation and measurement at high amplitudes. On the other hand, one would expect ΛL_N^2 to change with large amounts of deformation, especially when large amounts of cross-slip and tangling develop.

Thus, it seems probable that the beginning of cell structure formation should be observable in a decrease of the modulus defect as measured at high oscillating-stress amplitudes.

2. 2. 3. Comparison of Hasiguti and Bordoni Peaks in fcc Metals with Deformation-induced Peaks in Refractory bcc Metals

Hasiguti and his associates have made extensive studies of the damping peaks which occur at temperatures above the Bordoni peaks in plastically deformed fcc and hcp metals. In general, these peaks are less stable than the Bordoni peaks; occur in pairs or trios; have energies which lie in the range 0.2 to 0.6 ev and are roughly linearly related to the melting point of the metal; and have attempt frequencies which are several orders of magnitude smaller than those usually associated with simple atomic diffusion processes. The most detailed studies of this class of peaks have been the work of Okuda, (43) Okuda and Hasiguti (38) in Au and Cu in the 1 cps frequency range, and Koiwa and Hasiguti. (44)

Deformation of Au at 77.3°K produced a very large ($Q_m^{-1} \sim 1 \times 10^{-2}$ for 15 percent deformation) and unstable peak P_2 , which has an energy of ~ 0.3 ev and an attempt frequency of $\sim 3 \times 10^9 \text{ sec}^{-1}$. Isothermal measurements at the peak temperature, $\sim 180^\circ \text{K}$ (1 cps), showed that the peak first grew following deformation and then decayed, finally disappearing completely. Simultaneous with the growth of P_2 was a partial decay of the strength of the Bordoni peak. With the subsequent decay of P_2 , the Bordoni peak began increasing while two new smaller peaks, P_1 and P_3 , appeared on either side of the temperature of the P_2 peak. The maximum internal friction of P_1 never exceeded 1×10^{-3} for as much as 60 percent deformation, while P_3 reached a maximum of $\sim 2 \times 10^{-3}$ for ~ 15 percent and decreased for larger amounts of deformation.

With further annealing at 300°K , P_1 grew at first and then began to decay, while P_3 decayed from its first appearance.

Okuda and Hasiguti⁽³⁸⁾ found that the internal friction peaks in Cu deformed at 77.3°K behaved essentially in the same manner as those found in Au.

In both Au and Cu, the modulus is observed to increase irreversibly, first with the growth of P_2 , and then again with the growth of P_1 . Okuda and Hasiguti interpret this modulus increase to mean that dislocation pinning occurs during the growth of the peaks. They therefore associate the source of the mechanical relaxation responsible for P_1 and P_2 with the interaction between point defects produced during the plastic deformation and dislocations. In the terminology used in Section 2.1.3.2, these peaks could be considered to have either static or dynamic point-defect barriers. Okuda and Hasiguti⁽³⁸⁾ assumed that the barriers are dynamic, whereas Hasiguti⁽³⁵⁾ favors the static point-defect barrier.

Additional experimental evidence for the point-defect barrier hypothesis (either static or dynamic) is claimed by Koiwa and Hasiguti,⁽⁴⁴⁾ based on the observation that if, after P_1 or P_2 has grown to almost maximum peak height, the specimen is further deformed at 77.3°K , the height of these peaks is considerably reduced; the peaks then appear again after aging at or a little above room temperature. Hasiguti interprets these results as meaning that the dislocations are pulled away from the pinning points by the plastic deformation, resulting in free dislocations and free point defects, neither of which, by itself, will contribute to the peaks in the given temperature range. During the aging at room temperature, the free point defects and dislocations migrate together and again form the dislocation-point-defect relaxator which produces the relaxation peaks.

The only amplitude dependence reported by these workers is that of the peak P_3 . They found that the height of P_3 decreased slightly on increasing the strain amplitude from 2×10^{-6} up to 7.5×10^{-5} ; the peak also shifted (not more than 5°C) to lower temperatures.

Okuda⁽⁴³⁾ measured the effects of a series of low-temperature anneals on the size and shape of the Bordoni peaks, following plastic deformation at 4.2°K . He found that there are three annealing stages based on the occurrence of irreversible modulus increases as the temperature is raised. The first large modulus increase occurs in the temperature region from 75°K up to 120°K , which corresponds roughly to the high temperature side of the Bordoni peak as measured at 0.5 cps. This first annealing stage is attributed by Okuda to the rearrangement of dislocations which were "quenched" into high-energy positions during the liquid-helium deformation. At temperatures in the vicinity of the high-temperature side of the Bordoni

peak, dislocation segments can generate double kinks according to the Seeger model and escape over the entrapping Peierls potentials, thus accounting for the first annealing stage. The second annealing stage occurs between 150° and 200° K and again shows an irreversible increase in the modulus. The rapid growth of the internal friction peak P_2 occurs in this temperature interval and is presumably closely connected with the mechanism responsible for this second stage. The third stage occurs near 270° K; the growth of peak P_1 starts in this temperature interval and is also presumably connected with the mechanism responsible for the third annealing stage.

Further annealing at 300° K and above reverses the modulus increases and results in the Bordoni peaks increasing in size and reaching internal friction values of nearly 1×10^{-2} following anneals at 500° K for several hours. Finally, as the background internal friction increases with annealing near and past the recrystallization temperature, ⁽⁴⁵⁾ the peaks lose their characteristic shape.

Okuda considers both the second and third annealing stages to be due to the deformation-produced point defects migrating into dislocation lines, pinning them, and producing the modulus increases. He considers the second stage to be due to the migration and resultant pinning of dislocations by Au interstitials, and the third stage to be due to the migration of vacancies. The reversing of the modulus increases with higher-temperature anneals may be due to further rearrangement of dislocations ⁽⁴³⁾ or perhaps to a redistribution of pinning points along the dislocation, forming clusters of vacancies, etc., ⁽⁴⁶⁾ thus effectively reducing the pinning-point density along those dislocations which contribute to the Bordoni peaks.

An examination of the available energies for both the Bordoni and Hasiguti peaks shows that there is a tendency toward the high-melting-point metal having high energies for their Bordoni and Hasiguti peaks. Thus, since the refractory bcc metals possess very high melting points, it seems reasonable to expect that if these metals have counterparts to the Bordoni and Hasiguti peaks, the energies of these peaks may be higher than those found in the close-packed metals so far examined.

If the correspondence between the two metals holds, the α peak of Nb should rise strongly following deformation at liquid-nitrogen temperatures, analogous to the rise of the Bordoni peak in Au following deformation at liquid-helium temperatures. This expected result is confirmed, as discussed in Ref. 42. As the temperature is raised through the high-temperature side of the α peak, an increase in the modulus should be found corresponding to the first annealing stage seen in Au. This result is not found in Nb (see Ref. 42). Continuing the annealing to higher temperatures should result in the growth of one of the β peaks, and according to the Au and Cu

results, the analog to the P_1 peak should not yet be found. Contrary to this prediction, all of the β peaks and the γ peak in Nb appear to have formed upon deformation. All of the β peaks have been observed to decay upon reaching the temperature region from 350°K up to 420°K , or in the case of high purity Ta they remain relatively unchanged.

Koiwa and Hasiguti⁽⁴⁴⁾ found that in Cu, P_1 and P_2 are reduced in height by deformation at 77°K , and the peaks appear again after aging at 300°K or slightly above. In contrast to these results in Cu, the β_2 , β_3 , and γ peaks in Nb are enhanced by low-temperature deformation.

Swartz⁽⁴⁷⁾ deformed Cu 5 percent, then annealed it at 450°K to eliminate P_1 and P_2 ; the specimen was then strained 0.1% at 180°K . This deformation produced a large increase in the Bordoni peak, but failed to introduce either P_1 or P_2 . Chambers, et al.⁽⁴²⁾ deformed Nb 25% at room temperature and then annealed it at 500°K , which greatly reduced the α peaks and virtually eliminated the β and γ peaks. The specimen was then deformed 0.25% at 78°K . This deformation produced a large increase in the α peak as well as a large increase in both the β and γ peaks.

The Bordoni peaks grow with annealing at temperatures up to near the recrystallization temperatures, whereas the α peaks in Mo (see Ref. 1) are strongly reduced by anneals up to 800°C . The α peaks in Nb and Ta are likewise reduced by anneals up to temperatures at least as high as 500°C .

Thus, although the correspondences between the Bordoni and Hasiguti peaks in fcc metals and the deformation-induced peaks of the bcc metals appear reasonable on the basis of the distribution of the energies of the various peaks, the details of annealing are quite distinctly different in the two groups of metals.

On the strength of these differences in annealing behavior, it appears then that the β and γ deformation-induced peaks have their origins in mechanisms that are probably not the same as those responsible for the P_1 , P_2 , and P_3 peaks found in Cu and Au.

Martinet⁽⁴⁸⁾ has found a series of unstable damping peaks in the vicinity of 350°C for 1 cps measurements in plastically deformed W. Some of these peaks appear to grow and decay with various annealing treatments which are analogous to the Hasiguti peaks in fcc metals.

If this observation and classification is valid in W, then similar peaks should be found in the other refractory metals above the γ peaks.

2.2.4. The Significance of Aging Phenomenon

In the early studies of the Bordoni peak effects in fcc metals, the point was made that the temperature of the peak was insensitive to the existence of impurities on dislocation lines. It was mainly this point that cast doubt on one of the earliest models of the Bordoni peak, ⁽²⁰⁾ since this model explicitly expressed the energy of the peak in terms of the concentration of impurities on dislocation lines. The Seeger double-kink generation model was an attempt to provide a dislocation relaxation mechanism, which was essentially free of the dependence on impurities. However, with more detailed study of the Bordoni peaks in the fcc metals, small impurity effects become apparent. ⁽⁴⁹⁾

In contrast to the small decreases in the temperature of the Bordoni peak of fcc metals, resulting from interaction with impurities, the α peak in bcc Mo is decreased more than 50°K , from 122°K down to 70°K , through aging (see Ref. 1), while the peak height is decreased from 300 to 50×10^{-5} . In single-crystal Nb, aging results in the α peak shifting from 180°K down to 130°K , while the peak height decreases from 200 to 2×10^{-5} . From these two examples, it is clear that if aging in the bcc metals is due to the interaction of impurities with dislocations, then the α damping peaks in bcc transition metals and the Bordoni peaks in fcc metals differ significantly in their response to impurity interactions. It can be seen from these arguments that it is particularly important to establish the mechanism responsible for the aging seen in the bcc transition metals.

Three different models have been proposed to explain the reduction of the height and the temperature of the damping peaks in bcc metals with aging:

- a. The mutual annihilation of dislocation segments, together with a change in the Peierls potential through impurity interaction, proposed by Bordoni. ⁽⁵⁰⁾
- b. The annihilation of drag-producing vacancies which are attached to dislocation segments. The annihilation is accomplished by the diffusion of self-interstitials to the vacancies, where they combine with them to leave the dislocation free of the vacancy dragging points. This model is proposed by Martinet ⁽⁴⁸⁾ to explain the decay of a deformation-induced damping peak found at 300°C for 1 cps in W.
- c. The pinning of dislocation segments by the diffusion of impurity interstitials and deformation-produced point defects to the dislocation line, proposed by Chambers and Schultz. ^(40, 2, 1) It is assumed in this model that the mobility of dislocation segments is determined by some kind of periodic, intrinsic potential barriers

which determine the peak temperature. The peak height and, to a lesser degree, the peak temperature are determined by an average restoring stress which depends on the concentration and strengths of pinning points.

The first model is inconsistent with the evidence presented on Nb (see Ref. 42), in which a specimen that had previously been deformed 25% at room temperature had the α peak reduced by aging at 500°K for 1/2 hr. The specimen was then deformed a small amount ($\sim 0.25\%$) at 78°K, which resulted in restoring the peak to nearly former strength. The size of the restored peak is much too large to be attributable to the 0.25% deformation alone; thus, the specimen appears to possess a "memory" of its previous 25% deformation, which was not destroyed by the aging treatment.

It has been shown⁽⁴²⁾ that the application of high oscillating-stress amplitude reveals a large damping peak and modulus defect, even in specimens which had received an aging treatment. Such measurements are reversible in that following measurements at high amplitudes, the measurements made at low amplitudes still show the reduced peak heights due to the aging treatment. Thus, the application of high measuring amplitudes does not significantly alter the dislocation state. If the first model of aging were correct, it is difficult to see how the application of high oscillating-stress amplitude can recreate the dislocations annihilated during the thermal treatment, when the measurements are made at the low temperature of the α peak and the measuring stress is $\sim 1/10$ the yield stress at that temperature. It is also difficult to see how dislocations are then apparently "annihilated" upon making low-amplitude measurements.

According to the second model of aging, annihilation of the dragging points (vacancies) on the dislocation line by the diffusion of self-interstitials to the line should result in the suppression of the damping peak associated with the dragging process; however, the total modulus defect should increase since the dislocation lines are now freer to move in phase with the applied oscillating stress. Instead, the modulus defect is seen to decrease on aging.⁽⁴⁸⁾

According to the third model of aging, the reduction of the relaxation strength is attributable to point defects (such as interstitial impurities) diffusing to dislocation segments and pinning them. According to the three-well-potential model of aging outlined in Section 2.1.2.3, the addition of pinning points to the line segments increases the size of the side-well energy A , which decreases the relaxation strength as well as the effective activation energy $H-A$ for motion of the segment. The effectiveness of pinning on the size of the side-well energy A depends on the strength of pinning. For example, if the interaction between the pinner and the dislocation segment is small, as depicted in Fig. 32a, the dependence of A

Fig. 32--Depiction of interaction between pinner and dislocation line:
(a) loosely pinned; (b) tightly pinned

on the concentration C of pinners is weak; whereas if the interaction is large (Fig. 32b), then the dependence of A on C is relatively strong, and is given in Eq. (22). Thus, since impurity-dislocation interaction energies are generally almost an order of magnitude larger in bcc transition metals than in fcc metals, it is reasonable, from this model, to expect considerably larger dependence of the peak temperature on aging treatment in the damping peaks of the bcc transition metals than is found in the Bordoni peaks of the fcc metals. Another consequence of the pinning model of aging is that the amplitude-dependent effects become reversible, as described above, by making use of the soft-spring potential analysis of amplitude dependence (see Section 2.1.2.2). Thus, the pinning-point density in the aged state is high, making the relaxation strength, as measured at low oscillating-stress amplitudes, very small. As the amplitude of the oscillating stress is increased, the effective-stiffness coefficient of the average pinning potential decreases, allowing the relaxation strength to increase, which, in turn, leads to an enhancement of the relaxation peak. Upon reducing the amplitude, the effective-stiffness coefficient of the potential returns to its former value and the relaxation peak becomes small again. Of course, if the amplitude and the temperature of measurement are each high enough to allow diffusion of the pinning points along the dislocation line, a redistribution of these points may take place along the line^{(51)*} and change the pinning state of the sample. This could result in the damping peak becoming larger for small measuring amplitudes following a high-amplitude measurement. Such irreversible amplitude-dependent effects have been observed in Nb by Chambers, et al.⁽⁴²⁾

In the aging of Mo (see Ref. 1), there is evidence that the higher temperature components of the α peak age faster than the lower temperature components. This observation suggests the general possibility of non-homogeneous aging, whereby pinning reactions reduce the relaxation strength of some relaxation components faster than they do others.

Thus, it is evident that very careful measurements of the damping and modulus defect over large ranges of frequency, and preferably using

*The application of relatively high-amplitude oscillating stress may result in a change of state of pinning if the pinning points possess a high enough mobility along the dislocation line. Several authors have proposed (J. Weertman, private communication, 1955; and J. Marx, quoted in the thesis of D. N. Beshers, University of Illinois, 1955) that oscillating stress may result in a sideways redistribution of pinning points into groups of clusters along the dislocations. G. Alefeld (private communication, 1964) has suggested that the resulting increased pinning-point density at certain points on the dislocation would favor the emission of some of the pinning points back into the lattice, thus resulting in a net decrease in pinning points. Thus, some of the time effects resulting from high-amplitude oscillations in the bcc transition metals may have the same origins as the time effects seen in fcc and hcp metals (see Ref. 51).

the same measuring-stress distribution over the sample, are required to give information as to the details of the pinning mechanism responsible for the temperature shifts on aging in these metals.

The impurity responsible for the aging in the Nb and Ta experiments seems to be interstitial oxygen, since little aging is present in Ta specimens which exhibit no oxygen Snoek peak, whereas significant aging effects are evident when the oxygen Snoek peak is observable. In heavily deformed high purity Ta, there is some evidence that the defect responsible for recovery of resistivity⁽⁵²⁾ may also contribute to the irreversible modulus increase.

2.2.5. Discussion of Amplitude Dependence

In Refs. 2 and 42, it has been shown that the oscillating-stress-amplitude dependence in the bcc transition metals is influenced by aging treatments. Aging at 500°K for 1/2 hr, for example, can increase the stress amplitude at which a rapid increase in damping and modulus defect, or breakaway, occurs by as much as 20-fold in Nb. Since prestraining by very small amounts restores the original amplitude dependence, it seems reasonable to assume that aging serves to introduce pinning points on dislocation lines, while the application of stress serves to free dislocations from pinning points, or create new, relatively impurity-free dislocations. The pinners in Nb and Ta appear to be either self-interstitials or deformation-induced point defects, or both (see Section 2.2.4). The evidence described above concerning amplitude dependence in the bcc transition metals appears to be explained by two different kinds of amplitude-dependence models. The well-known Koehler-Granato-Lücke (KGL) model and its modifications⁽⁵³⁾ may offer an explanation of the amplitude dependence seen in the high-temperature ranges (e. g., above ~350°K for 1 cps measurement in Nb); however, this kind of model is unable to account for the amplitude dependence existing at lower temperatures. The amplitude dependence which exists from liquid-helium temperatures up to ~350°K for measurements made at ~1 cps to resemble stress-enhanced relaxations, rather than the quasi-static hysteresis mechanism involving the catastrophic breakaway of dislocations from pinning points and their subsequent repinning. The main evidence against the application of the breakaway model to the low-temperature data is the size of the ratio of the amplitude-dependent modulus defect to the amplitude-dependent damping.

The KGL breakaway model predicts that this ratio is of the order of unity, whereas for Nb and Ta it is regularly between 5 and 10 at temperatures between 100°K and 350°K. On the other hand, the stress-enhanced relaxation model of amplitude dependence discussed in Section 2.1.2 predicts such a ratio if the high-amplitude damping is identified with the thermally activated relaxation damping measured at low amplitudes. In

that model, the high oscillating stress serves to decrease the effective restoring stress of the relaxators, which in turn results in increased relaxation strength and hence increased damping and modulus defect. Another prediction of the stress-enhanced relaxation model is that the damping on the high-temperature side of an enhanced peak is smaller than at the peak, whereas the breakaway model predicts a monotonic increase of high amplitude damping with increase in temperature. Much of the amplitude-dependent data in the vicinity of the α peaks does, in fact, show a slight reduction in the damping on the high temperature side of the peak; the reduction cannot, however, be expected to be a large effect since the β peaks tend to occupy much of the high temperature side of the α peak.

At temperatures above $\sim 350^\circ\text{K}$ for measurements made at ~ 1 cps in Nb and Ta, the ratio of the amplitude-dependent modulus defect to the damping approaches unity, suggesting the application of the KGL model in this temperature region. However, in all temperature ranges, both the damping and the modulus defect show the strong frequency dependence characteristic of thermally activated processes. Thus, the static hysteresis mechanism cannot be applicable without modification to include thermal activation. Furthermore, the absence of butterfly-shaped microstress-strain loops⁽⁵⁴⁾ suggests that the simple breakaway and repinning cycle assumed by the KGL model is not applicable to these metals.

One of the most interesting amplitude-dependent phenomena seen in the bcc transition metals is the existence of saturation in both the damping and modulus defect, with increasing stress amplitude, at temperature below $\sim 250^\circ\text{K}$ for measurements made at ~ 1 cps.

Furthermore, for large enough amplitudes ($> 4 \times 10^{-4}\text{G}$), both the damping and modulus defect decrease with increasing amplitude. The reduction of the modulus defect is considered to be particularly interesting since it suggests the existence of some kind of barriers restricting the amount of the motion of certain parts of the dislocation network. The reduction in the relaxation strength of the α peak with amplitudes in excess of 4×10^{-4} is clearly shown in Fig. 30 for high purity Ta. The shifting of the peak position toward lower temperatures suggests stress-assisted reduction of the activation energy of the α peaks. Perhaps the clearest evidence of restricted dislocation motion is shown in Fig. 33 for deformed Nb. The normalized dislocation strain obtained by the constant-temperature-rise strain-relaxation method shows a reduction for increasing stresses in the temperature range 120°K to 200°K . Only when the stress becomes so large that the β process is stress-assisted to temperatures near the α process does the modulus-defect stiffening effect disappear.

Thus, the restricting barrier for α dislocation motion appears to be the β process; at low stresses, only short range α dislocation motion is possible at temperatures below the β process. At sufficiently high stresses,

Fig. 33--Normalized strain relaxation $\epsilon_d/\epsilon = \Delta M/M$ for 20 percent deformed Nb; measurement made at various applied stresses in stress range that shows restricted relaxations

longer range dislocation motion is possible since the β process no longer acts as a barrier to α dislocation motion. Thus long range dislocation motion appears to act like a flow process through resistive elements connected in series, wherein the slowest process effectively determines the total flow. In the refractory bcc metals Nb and Ta, it appears that the most resistive element in the room-temperature range is the β process, while below liquid-nitrogen temperatures, the most resistive element is the α process. This follows from a two-component-series flow model in which the rate of flow (strain rate) of each component is determined by a stress-assisted mobility term such as given by Eq. (9a) where $H_\alpha < H_\beta$ but $v_\alpha \ll v_\beta$. Thus, at temperatures below the α process, even though the α process possesses a lower energy than the β process, the larger stress coupling factor (activation volume v_β) of the β process enables the applied stress to make the effective energy of the β process smaller than the α process.

2. 3. CONCLUSIONS AND SUGGESTIONS FOR FURTHER INVESTIGATION

From the foregoing relaxation studies it appears that the motion of dislocations in the bcc transition metals is controlled by thermally activated processes possessing an energy spectrum with a number of broad bands. There is evidence that the activation energy of some of these bands may be reduced by the application of stress, i. e., that the thermal activation event may be stress-assisted. Furthermore, the highest energy process appears to possess the largest rate of energy reduction by stress or activation volume.

The interstitial impurity, oxygen, in low concentration (<1 at. ppm) can effectively immobilize or pin dislocations in Ta and Nb. The effectiveness of pinning on various parts of the energy spectrum is not uniform; the lower energy parts of the spectrum are more resistant to pinning.

If the results on high purity Ta are representative of the other bcc transition metals, deformation is not essential to produce dislocation relaxations in these metals. Ta annealed at 2500°C for one hour shows a dislocation-relaxation spectrum if measured in the stress-amplitude-dependent region. Prestraining enhances the saturation relaxation strength of the lower-temperature relaxations (α' and α) by a factor of only 3 or 4; and extensive prestraining can strongly reduce the relaxation strength of these processes.

The amplitude dependence observed in these metals cannot be explained by a static hysteresis model. Most of the available evidence indicates that the stress-amplitude-dependent part of the internal friction and modulus defect is a stress-enhancement of the amplitude-independent,

thermally activated relaxation process. The stress serves to decrease the effective stiffness of the dislocation relaxation, thus increasing the relaxation strength. The multiplicity and broadness of the stress-enhanced dislocation relaxations tend to make the amplitude-dependent internal friction and modulus defect appear to be frequency independent. However, careful examination over five orders of magnitude of frequency shows that the nonlinear components are indeed frequency dependent and can be expressed as broad, thermally activated, and, at high stresses, stress-assisted relaxations. Also, direct examination of the microstress-strain loops⁽⁵⁴⁾ has failed to show any evidence of the "butterfly" loops predicted by a breakaway model based on static hysteresis.⁽⁵⁵⁾

In all cases of annealed or deformed specimens, the α' and α parts of the relaxation spectrum behave like constrained relaxators, i. e., both the internal friction and the modulus defect saturate and decrease with increasing oscillating stress; whereas the higher energy parts of the spectrum, β and γ , behave more like unconstrained relaxators, i. e., the internal friction appears to increase monotonically with increasing stress.

It is felt that the constrained behavior of the lower energy processes provides an important clue to the nature of the dislocation mechanism associated with these processes. If the α' and α dislocation processes are coupled in series with the β and γ dislocation processes, the motion of the lower energy processes will be limited by the motion of the higher energy processes. Thus, the restricted nature of the α' and α relaxations follows from such an assumption, because at a temperature and frequency at which the β and γ relaxators are frozen, the α' and α relaxators can undergo limited movement; but the frozen β and γ processes provide barriers to extensive motion. Therefore, the stiffness of the α' and α processes will increase with increasing displacement, requiring higher stresses for further motion until the stress becomes large enough to "unfreeze" the β process through the stress-assist mechanism.

The CTRSR measurements show that long-range dislocation motion is governed either by the highest energy β relaxations or the γ relaxations.

Using these observations, it is useful to investigate the consequences of certain models.

- a. Assume the α peaks are analogous to the Bordoni peaks in fcc metals and the Bordoni peaks represent double-kink generation in edge and screw dislocations. If this assumption is made, then it follows from the above observations that the long-range dislocation motion in bcc transition metals at intermediate temperatures is not determined by the Seeger mechanism, as Conrad⁽⁵⁶⁾ and others have stated. Some other process or

processes, such as conservative jog motion, will determine the long range motion.

- b. Assume α peaks represent double-kink generation in edge-type dislocations only; and the β peaks represent thermally activated processes associated with the motion of screw dislocations. Long-range dislocation motion would require that the α and β processes be series-coupled since no dislocation multiplication could take place until the screws could move.

A number of other possibilities exist, based only on the observation of the restricted nature of the lower temperature processes. The annealing behavior of the various peaks, sensitivity to deformation, frequency dependence of the relaxation strength, and pre-exponential size should provide additional useful information about the details of the dislocation mechanisms operating in these metals.

It is clear that relatively little is known about those parameters that can be measured, such as the energy and pre-exponentials in the same deformed and aged specimens, as well as the frequency dependence of the relaxation strengths. These measurements are very difficult to make, requiring wide frequency ranges because of the multiplicity of relaxation times involved and the necessity of having the stress distribution essentially the same as the frequency is varied. Very low frequency measurements using high-sensitivity detection methods can be used to particular advantage in these measurements.

Much can be learned from combining low amplitude with high amplitude measurements, and especially by combining them with some kind of measurement that involves long-range dislocation motion such as creep.

Especially needed are acoustical experiments using well-defined dislocation arrays, such as can be produced by controlled bending of single crystals. Such measurements should be of great help in learning to recognize the type of relaxation signal to be expected from a known type and configuration of dislocation.

REFERENCES

1. Chambers, R. H., and J. Schultz, Acta Met. 10, 466 (1962).
2. Chambers, R. H., and J. Schultz, Acta Met. 8, 585 (1960).
3. Snoek, J. L., Physica 8, 711 (1941).
4. Seeger, A., P. Schiller, and H. Kronmüller, Z. Naturforsch. 159, 740 (1960).

5. Seeger, A., P. Schiller, and H. Krönmüller, Phil. Mag. 5, 85 (1960).
6. Schiller, P., H. Krönmüller, and A. Seeger, Acta Met. 10, 67 (1962).
7. Seeger, A., N. Donth, and F. Pfaff, Discussions Faraday Soc. 23, 19 (1957).
8. Schoeck, G., and A. Seeger, Acta Met. 7, 469 (1959).
9. Kessler, J. O., Phys. Rev. 106, 646, 654 (1957).
10. Chambers, R. H., J. Appl. Phys. Letters 2, 165 (1963).
11. DeBatist, R., Phys. Status Solide 2, 661 (1962).
12. Koehler, J. S., Imperfections in Nearly Perfect Crystals, John Wiley and Sons, New York, 1952, Chapter VII, p. 197.
13. Rogers, D. H., J. Appl. Phys. 33, 781 (1962).
14. Swartz, J. C., and J. Weertman, Acta Met. 10, 448 (1962).
15. Nowick, A. S., Prog. Metal Phys. 4, 1 (1953).
16. Friedel, J., in Creep and Fracture of Metals at High Temperatures, proceedings of a symposium held at the National Physics Laboratory, Teddington, England, 1963, H. M. Stationery Office, 1963, p. 409.
17. Weertman, J., J. Appl. Phys. 28, 193 (1957).
18. Pare, V. K., J. Appl. Phys. 32, 332 (1961).
19. Alefeld, G., Z. Physik 170, 249 (1962).
20. Mason, W. P., J. Acoust. Soc. Am. 27, 643 (1955).
21. Donth, H., Z. Physik 149, 111 (1957).
22. Cottrell, A. H., Dislocations and Plastic Flow in Crystals, Oxford Press, London, 1953.
23. Seeger, A., and P. Schiller, in Physical Acoustics, W. P. Mason, Ed., Academic Press, New York: (in press), Vol III-A, Chap. 6.
24. Lothe, J., and J. P. Hirth, Phys. Rev. 115, 543 (1959).
25. Lothe, J., Phys. Rev. 117, 704 (1960).
26. Brailsford, A. D., Phys. Rev. 122, 778 (1961).
27. Seeger, A., and P. Schiller, Acta Met. 10, 348 (1962).
28. Southgate, P. D., and A. E. Attard, J. Appl. Phys. 34, 855 (1963).
29. Mason, W. P., Acta Met. 10, 195 (1962).
30. Seeger, A., Phil. Mag. 1, 651 (1956).
31. Hirsch, P. B., Phil. Mag. 7, 67 (1962).

32. Feltham, P., Phil. Mag. 6, 1301 (1961).
33. Schoeck, G., Acta Met. 9, 382 (1960).
34. Bruner, L. J., Phys. Rev. 118, 399 (1960).
35. Hasiguti, R. R., "Internal Friction Due to Diffusion of Dislocation-Kinks Trapped by Point Defects," in J. Phys. Soc. Japan 18, Suppl. 3 (1963); proceedings, International Conference on Crystal Lattice Defects, Tokyo, 1962.
36. Cottrell, A. H., and M. A. Jaswon, Proc. Roy. Soc. (London) A119, 104 (1949).
37. Schoeck, G., Acta Met. 6, 617 (1963).
38. Okuda, S., and R. R. Hasiguti, Acta Met. 11, 257 (1963).
39. Gilman, J., in J. Phys. Soc. Japan 18, Suppl. 3 (1963); proceedings, International Conference on Crystal Lattice Defects, Tokyo, 1962.
40. Chambers, R. H., and J. Schultz, Phys. Rev. Letters 6, 273 (1961).
41. Schultz, J., and R. H. Chambers, Bull. Am. Phys. Soc. 9, 214 (1964).
42. Chambers, R. H., in Physical Acoustics, W. P. Mason, Ed., Academic Press, New York (in press), Vol. III-A, Chapt. 5.
43. Okuda, S., "Study of the Bordoni Peak in FCC Metals after Deformation at 4,2°K and Subsequent Low Temperature Annealing," in J. Phys. Soc. Japan 18, Suppl. 3 (1963); proceedings, International Conference on Crystal Lattice Defects, Tokyo, 1962.
44. Koiwa, M., and R. R. Hasiguti, Acta Met. 11, 1215 (1963).
45. Niblett, D. H., and J. Wilks, Advan. Phys. 9, 1 (1960).
46. Coulomb, P., and J. Friedel, "On the Formation of Cavities Along Dislocations," in Dislocations and Mechanical Properties of Crystals, International Conference, Lake Placid, 1956, John Wiley and Sons, New York, 1957, p. 55.
47. Swartz, J. C., Acta Met. 10, 184 (1962).
48. Martinet, B., Thesis for Ecole Polytech de l'Université de Lausanne, 1964.
49. Niblett, D. H., in Physical Acoustics, W. P. Mason, Ed., Academic Press, New York (in press), Vol. III-A, Chap. 1.
50. Bordoni, P. G., U. S. Department of the Army, E.R.O. Contract Report DA91-591-EUC-2051, 1963.

51. Chambers, R. H., and R. Smoluchowski, Phys. Rev. 117, 725 (1960).
52. Peacock, D. E., Thesis, Imperial College, London, 1961.
53. Granato, A., and K. Lücke, in Physical Acoustics, W. P. Mason, Ed., Academic Press, New York (in press), Vol. III-A, Chap. 3.
54. Chambers, R. H., H. Harper, and J. Filloux, (to be published).
55. Granato, A., and K. Lücke, J. Appl. Phys. 27, 583 (1956).
56. Conrad, H., Phil. Mag. 5, 745 (1960).

III. STORED-ENERGY RELEASE IN IRRADIATED MOLYBDENUM

An effort has recently been undertaken to measure the stored-energy release in specimens of irradiated molybdenum supplied by Hanford Laboratories. Four stored-energy-release experiments on irradiated specimens have been conducted with emphasis on extending the measurements to temperatures of 700°C or higher. Data reduction is currently in progress, and the following report provides an indication of results as they are presently in hand.

3.1. EXPERIMENTS

The calorimetric method of quantitative differential thermal analysis (QDTA) employed in these investigations has been treated in a recent publication⁽¹⁾ and has been described in greater detail in a previous report.⁽²⁾ The modifications made to extend the technique to the temperatures required to observe the stored energy of recrystallization in cold-worked iron were given in the last annual report.⁽³⁾ In the present work the emphasis on extending the measurements to higher temperature is continued in order to observe as many thermally activated defect reactions as possible.

A theoretical analysis of the QDTA method shows that the sensitivity is directly dependent on the thermal lag of the specimens behind the calorimeter block and that the precision is directly dependent on the degree to which the block temperature measurement is accurately representative of the temperature distribution over the interior surface of the block. The first step in extending the QDTA method to higher temperatures was to replace the copper calorimeter block by a molybdenum block of slightly smaller dimensions. In view of the lower thermal conductivity of molybdenum, it was necessary to place taps on various segments of the block heater in order to trim the power input to give a more uniform temperature distribution. This trim was adjusted to give $T_w - T_r = 0$ (where T_w is wall temperature of the block as sensed by a Chromel-Alumel thermocouple junction placed halfway up the interior surface of the calorimeter block, and T_r is the temperature of the reference specimen) at the maximum block temperature of 1000°C.

No attempt has been made as yet to calibrate the specimen inter-coupling factor f with the cell geometries employed in the present work. The results reported below employ the value $f = 0.075$, derived from the previous work on stored-energy release in deformed copper and iron.

Two irradiated molybdenum specimens were supplied by Dr. H. E. Kissinger of Hanford Laboratories. A vendor's analysis of the material is given in Table 4. The specimens were irradiated to fast-neutron exposure ($E > 1$ Mev) of 10^{18} nvt and 10^{19} nvt at temperatures of about 40°C . Cold-worked and annealed specimens were provided for preliminary test runs and for the annealed reference specimen. No calorimetric difficulties were encountered in working with the specimens at the modest levels of radioactivity displayed by these specimens.

Table 4
ANALYSIS OF MOLYBDENUM SPECIMEN

Element	Concentration (ppm)	Element	Concentration (ppm)
Al	<10	Mn	<10
Ca	20	Sn	<10
Si	10	Mg	<10
W	100	C	<10
Fe	10	O ₂	6 to 11
Cr	<10	N ₂	4 to 8
Ni	<10	H ₂	1 to 2
Cu	10		

The specimens were provided in the form of rods 2 in. long and 3/8 in. in diameter, with hemispherical ends. Because this specimen geometry is unsuitable for direct use in the differential calorimeter, the specimens were cut into two nearly identical bullet-shaped specimens 1 in. in length. Calorimeter cells were prepared to accept these specimens with the hemispherical ends facing up and with the flat ends directly in contact with the thermocouple junctions. In order to minimize the thermal inertia of these relatively small cell-specimen combinations, the hemispherical top of the specimen was not enclosed by the cell.

3.2. RESULTS

The results for two stored-energy-release experiments are given in Figs. 34 and 35 in terms of the Q' function, which is a convenient plotting function defined by

$$Q' = - \frac{1}{1 - \frac{e_s - e_r}{e_w - e_r}} \sum_s^n \frac{n_s c_i}{n_i c_i} \frac{dE_s}{dT_r} + \beta' \quad (1)$$

Fig. 34--Stored-energy release in molybdenum irradiated to 10^{18} nvt at 40°C

Fig. 35--Stored-energy release in molybdenum irradiated to 10^{19} nvt at 40°C

where dE_s/dT_r is the stored-energy release as a function of the temperature of the reference specimen and β' is the base-line difference in thermal couplings of the reference and test specimens with the calorimeter block. The differential electromotive forces measured by the differential thermocouples are represented by $e_s - e_r$ and $e_w - e_r$, n_s is the number of gram-atoms in the test specimen, and $\sum_s n_i c_i$ represents the total thermal inertia (heat capacity) of all components thermally associated with the test specimen. Q' is given in terms of the measurables by

$$Q' = \frac{(1 + 2f) \left(\frac{e_s - e_r}{e_w - e_r} \right) + \frac{d(e_s - e_r)}{de_r}}{1 - \frac{e_s - e_r}{e_w - e_r}} \quad (2)$$

Thus, the stored-energy release is given by the difference between Q' plots obtained under identical heating conditions.

The data presented in Figs. 34 and 35 were obtained with a heating rate of $200 \mu\text{v}/\text{min}$ with a Chromel-Alumel thermocouple; this corresponds to an approximate temperature rise of $5^\circ\text{C}/\text{min}$. The runs were extended to 1000°C , but the data are not given above 870°C owing to the increasingly erratic behavior of the base lines above this temperature. However, it should be noted that no evidence of large energy release (i. e., comparable to the release peaks evident at lower temperatures) was observed above 870°C .

The results show some base-line displacement and a base-line uncertainty which increases with temperature. However, the duplicate runs show excellent reproducibility in respect to the general shape of the release peaks.

Only preliminary estimates are available, at this stage in data reduction, for the areas under the release peaks. The peak at 222°C for the low-dose specimen represents approximately 15 cal/g-atom, and a small smeared-out release is possibly evident near 650°C . The peaks at 205°C and 685°C for the high-dose specimen represent approximately 40 and 25 cal/g-atom, respectively. These values for the low-temperature peaks are consistent with the earlier observations of Kinchin and Thompson, (4) whose measurements were not extended above 280°C .

The results on the higher-dose specimens also suggest three additional release peaks and the possibility of a "garbage-annealing," which could be a merging of various annealing processes. In view of the base-line uncertainties, the existence and magnitude of these stored-energy

releases should be resolved by further work, e. g., by interrupting a release run to enable the initiation of energy release at higher temperatures to be observed in a subsequent run where the lower-temperature base line is clearly defined.

REFERENCES

1. White, J. L., and K. Koyama, "The Application of Differential Thermal Calorimetry to Measurements of Stored-Energy Release in Metals," Rev. Sci. Instr. 34, 1104-1110 (1963).
2. White, J. L., and K. Koyama, "The Application of Differential Thermal Calorimetry to Measurements of Stored-Energy Release in Metals," USAEC Report GA-2732, General Atomic Division of General Dynamics Corporation, August 6, 1962, 24 p.
3. Chambers, R. H., T. A. Trozera, and J. L. White, "A Program of Basic Research on Mechanical Properties of Reactor Materials," Summary Report, USAEC Report GA-4900, General Atomic Division of General Dynamics Corporation, September, 1963, 62 p.
4. Kinchin, G. H., and M. W. Thompson, "Irradiation Damage and Recovery in Molybdenum and Tungsten," J. Nucl. Energy 6, 275-84 (1958).