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THE EFFECT OF NITROGEN ON THE STRENGTH OF
THORIUM

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The effect of nitrogen on the strength of thorium

by

David Robert McLachlan

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The effect of nitrogen on the strength of thorium*

David Robert McLachlan

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The flow stress of the thorium-nitrogen alloys containing 0.16 a/o to 0.97 a/o nitrogen was measured over a temperature range from 4.2°K to 873°K. Constant strain rate and constant stress measurements of the flow stress were made at strain rates ranging from 10^{-12} to 10^{-3} per second. It was found that the flow stress could be divided into a thermally activated and an athermal stress component. The thermally activated component increased linearly with nitrogen content from 198°K to 360°K and increased with the square root of nitrogen content at 77°K and 4.2°K. The athermal component was found to be nearly independent of nitrogen content and temperature. The strengthening of thorium by nitrogen was primarily due to a strong interaction between randomly distributed nitrogen atoms and glissile dislocations.

Age hardening could be produced in thorium-nitrogen alloys which were above the solubility limit of nitrogen in thorium. The aged alloys contained thorium nitride particles

less than 10 atom diameters, $36\text{\AA}$, in size which greatly increased the flow stress of the metal. The temperature and strain rate dependence of the flow stress were used to determine the activation energies and activation volumes of the rate controlling processes.

INTRODUCTION

Background

Our modern civilization is vitally dependent on the mechanical properties of metals. In the past years, a great deal of knowledge has been accumulated about the ways in which the various structural parameters (defects, impurities, atomic forces, etc.) affect the strength of metals. A large part of this knowledge has been derived from a better understanding of plastic deformation in terms of dislocation movement and dislocation interactions with various defects. As a result, the relation between the various dislocation mechanisms and mechanical properties is now better understood. One goal of investigations concerned with dislocation mechanics is to obtain a basic understanding of the plastic characteristics of the material in terms of dislocation behavior. From this knowledge, new concepts may be formulated and eventually utilized in engineering applications or form the basis for the development of new and superior alloys.

One of the important effects of alloying on the mechanical properties of metals is to raise the yield stress and increase the strength of the metal. The effect of an alloying element will depend on the form in which it is present. Generally, it has the smallest effect on strength when present in coarse well-separated particles of precipitate, the largest effect when in the form of a finely dispersed precipitate and

an intermediate effect when present in solid solution.

It is generally accepted that the stress needed to cause plastic flow is due to obstacles impeding the motion of the dislocations through the crystal. These obstacles can be divided into two groups depending on the distance over which they interact with mobile dislocations. The short range obstacles to plastic flow can be overcome by thermal fluctuation aiding the applied stress, even though the force on the dislocation is smaller than the force exerted by the obstacles. This type of interaction will lead to a temperature and strain rate dependence of the flow stress. These short range obstacles are limited in size to a diameter of a few (<10) interatomic distances. If an obstacle is large enough so that thermal fluctuation cannot assist the applied stress in overcoming it, it is considered to be a long range obstacle. The stress resulting from long range interaction between obstacles and dislocations would be independent of strain rate and only dependent on temperature due to the temperature dependence of the elastic moduli. The flow stress of a metal can then be considered to consist of two components, the athermal σ_{μ} and the thermally activated component σ^* , i.e. $\sigma = \sigma^* + \sigma_{\mu}$. Experimental results show that either σ^* or σ_{μ} or both can be influenced by the addition of alloying elements.

The long range or athermal obstacles, which are not affected by random thermal energy fluctuations, are believed

to be due to other dislocations on parallel slip planes, large precipitate or second-phase particles and grain boundaries, although all the contributions to the athermal component are not yet clear.

A number of thermally activated dislocation mechanisms have been proposed to account for thermal obstacles in pure metals. These include overcoming the Peierls-Nabarro stress, intersection of forest dislocations, nonconservative motion of jogs in screw dislocations, and climb of edge dislocations. If impurity atoms are added to metals their effect on the above mechanisms must be taken into account, as well as the interactions between dislocations and impurity atoms. As early as 1925, Becker (1) recognized the dynamic nature of plastic deformation and suggested that thermal fluctuation assisted the applied stress in overcoming obstacles to plastic flow and applied an Arrhenius type relation to plastic deformation.

The basic equation which is generally used in a study of dislocation dynamics is:

$$\dot{\epsilon} = K \rho b \bar{v} = K \rho b s v^* \exp\left(-\frac{\Delta H(\sigma^*)}{kT}\right) \quad (1)$$

where $\dot{\epsilon}$ is the tensile strain rate, K is a constant relating shear strain to tensile strain, i.e. $\epsilon = K\gamma$, ρ is the density of dislocations participating in the deformation, b is the Burgers vector and $\bar{v}$ is the average velocity of the dislocations. The term s is the product of the number of places where

thermal activation can occur per unit length of dislocation, the area swept out per successful thermal fluctuation and the entropy of activation and v^* is the frequency with which a dislocation attempts to overcome the obstacles against which it is pressed by the applied stress (2). ΔH is an activation energy (enthalpy) which decreases with the thermally activated component of flow stress σ^* .

An expression for the activation energy was developed by Conrad and Wiedersich (3)

$$\Delta H(\sigma^*) = -kT^2 \frac{\left(\frac{\partial \sigma}{\partial T}\right) \dot{\epsilon} - \frac{\sigma_{\mu}}{\mu} \frac{d\mu}{dT}}{\left(\frac{\partial \sigma}{\partial \ln \dot{\epsilon}}\right)_T} \quad (2)$$

where μ is the shear modulus, σ is the observed flow stress, σ_{μ} is the athermal stress and $\dot{\epsilon}$ is the strain rate. Conrad (4) later defined an activation volume as

$$v^* = kT \left(\frac{\partial \ln \dot{\epsilon}}{\partial \tau} \right)_T, \quad (3)$$

where v^* , the activation volume, is a measure of the volume over which the thermal process occurs and τ is shear stress.

The calculation of activation energy and activation volume has been used in the study of plastic deformation to aid in identifying the dislocation mechanism which is rate controlling under specific conditions of temperature and strain rate. The theory and experimental techniques for evaluation of the deformation parameter needed to identify the rate-controlling dislocation mechanism are described by

a number of authors: Basinski (5), Conrad (4), Gregory (6) and Li (7).

One of the distinguishing characteristics between the body-centered cubic (bcc) metals and the close packed metals (hexagonal close packed, hcp, and face-centered cubic, fcc) is the strong temperature and strain rate dependence of the flow stress in bcc metals. The flow stress of bcc metal increases sharply at low temperatures while the flow stress of close-packed metals varies only slightly from room temperature to absolute zero. The strain rate parameter, $\Delta\sigma/\Delta\ln\dot{\epsilon}$, for body centered cubic metals increases with decreasing temperature, goes through a maximum, and then decreases, approaching zero as the temperature goes to absolute zero. In face centered cubic metals, the strain rate parameter generally remains small and nearly constant with temperature.

Solid Solution Strengthening

Solid solutions may be classified into either of two distinct types. The first is known as a substitutional solid solution in which the solute atom takes a lattice position which normally is occupied by solvent atoms. The other type of solid solution is known as an interstitial solid solution. Here the solute atom does not displace a solvent atom but rather enters one of the holes between the solvent atoms. Carbon, nitrogen, oxygen, hydrogen and boron are the most common interstitial solute atoms in crystalline metals.

The introduction of solute atoms into metal crystal lattices almost always produces an alloy which is stronger than the pure metal but the strengthening mechanism is apparently not the same in all cases. Consequently, there are a number of theories on solid solution hardening. These appear to fall into two categories; one deals with hardening sources which are partially or totally removed by strain, while the other category deals with frictional mechanisms, whereby the solute produces a resistance to dislocation movement which is unaffected by strain.

Cottrell (8,9) suggested that solute atoms in solid solution would not be randomly distributed, but would tend to segregate around dislocations. Around an edge dislocation, the atoms above the slip plane are in compression and below it are in tension. The strain energy resulting from this stress field can be reduced by large solute atoms collecting in the expanded or tension region and small solute atoms collecting in the compressed region. Since the energy is lower when a dislocation is surrounded by a solute atmosphere, a higher stress is required to move the dislocation away from the solute atmosphere. After the dislocation is moved or unpinned, it then can move at a lower stress.

In a face-centered cubic metal, dislocations on a (111) plane can split into two partial dislocations. In the region between the partial dislocations there is a strip of stacking fault, i.e., a layer about two to three atoms thick where the

crystal structure is close-packed hexagonal. Suzuki (10) rationalized that, since the cohesive energy between atoms in the stacking fault differs from that in the surrounding face-centered cubic material, the concentration of the solute atoms in the stacking fault should differ from that of the average concentration. This segregation of solute or solvent atoms in the stacking fault can result in pinning of the dislocation.

There is a third strengthening mechanism which is affected by strain, that due to short range order hardening as proposed by Fisher (11). In a solid solution the solute atoms may be arranged in a random manner or in a regular or ordered pattern. An ordered region in a solid solution crystal has the solute and solvent atoms arranged in a specific pattern on the periodic lattice positions. This ordering is caused by a preference for the formation of solute-solvent atomic bonds and is a lower energy state than the disordered arrangement. If an alloy has some local order, the passage of a dislocation through the ordered region will lower the degree of order and produce a more nearly random configuration of higher energy, resulting in a higher yield stress. When the ordered structure is destroyed the dislocation can then move at a lower flow stress.

There are at least seven "frictional" mechanisms by which the resistance to dislocation movement could possibly be explained. These are; the Peierls-Nabarro stress, the Snoek

effect, electrical interaction, Mott-Nabarro hardening, modulus interaction, combined size and modulus effect, and the Bond Energy model.

The interatomic configuration surrounding a dislocation is periodically altered as the dislocation moves along the slip plane. These atomic rearrangements cause a change in the energy associated with the dislocation, and, as a consequence, the dislocation experiences a resistance to its movement. The determination of the magnitude of the shear stress needed to overcome this drag or lattice friction was first calculated by Peierls (12) and Nabarro (13). The Peierls-Nabarro stress was shown to vary exponentially with a/b , i.e.

$$\tau = \frac{2\mu}{1-\nu} \exp\left[-\frac{2\pi a}{b(1-\nu)}\right], \quad (4)$$

where μ is the shear modulus, b is the Burgers vector, ν is the Poisson's ratio and a is the interplanar spacing. The ratio a/b is greater for face centered cubic metals than it is for body centered cubic metals. The result is that the Peierls-Nabarro stress will be greater for body centered cubic metals than for face centered cubic metals. Thermal fluctuations may aid the applied stress in forming kinks in the dislocations. These kinks expand under the applied stress and thereby advance the dislocation one atomic distance. In a review article, Conrad (14) concluded, from the data on body-centered cubic metals, that the temperature and strain rate dependence of the flow stress is due to the Peierls-Nabarro

resistance to dislocation glide. This conclusion was based on the fact that the experimentally determined values of the activation energy and activation volume were independent of structure, impurity content, strain and method of determination for a given metal.

Another type of "frictional" resistance to dislocation movement which is important in body-centered cubic metals is that due to the Snoek effect (15). In body-centered cubic metals, interstitial atoms occupy octahedral sites, located at the centers of the cube edges or at the centers of the cube faces. These sites are crystallographically equivalent, but they have a distorted symmetry in which two of the solvent atoms are nearer to the center of the site than the other four nearest neighbor atoms. An interstitial atom in the octahedral site displaces these two solvent atoms more than the other four atoms and thereby gives rise to a tetragonal distortion. Under an applied stress, the unit cube becomes elongated in one direction and the interstitial atoms will prefer those octahedral sites for which the applied stress already produces a distortion similar to that produced by their presence. Consequently, near a dislocation, the interstitial solute atoms are not randomly distributed, but prefer those sites which lower the combined strain energy of the interstitial atom and dislocation. The Snoek effect produces a frictional force on a moving dislocation because, as it passes near an interstitial atom, the atom will tend to jump into a

preferred site. This local ordering places the dislocation in an energy well and leads to a higher flow stress.

An edge dislocation will carry a slight negative charge in the dilated region and a slight positive charge in the compressed region, resulting in a weak electrical line dipole (16). Consequently, an electrical interaction could exist between the dislocations and foreign atoms carrying a net charge. In experiments (17,18) conducted on copper based solid solutions, it was found that electrical interaction appeared to be an important strengthening factor because similar stress-strain curves were obtained for alloys with equal electron to atom ratios. However, the flow stress was not proportional to the electron to atom ratio for the copper-tin alloys, which had a higher yield strength but a lower electron to atom ratio than the other alloys.

Mott and Nabarro (19,20) developed one of the first theories on simple solid solution hardening. They assumed that solid solution strengthening resulted from the interaction of randomly distributed solute atoms with moving dislocations. This interaction was due to the local internal stress field resulting from the size difference between the solute and solvent atoms. Two expressions were derived for calculating the flow stress; the essential difference between them was the degree to which the moving dislocation was allowed to bend. Both expressions predicted a linear increase

of the flow stress with concentration. McLean (21) and Cottrell (8) compared experimental results with calculations made using the Mott-Nabarro theory based on the size difference for various metals and found that the predicted values were generally high by about a factor of ten. Cottrell concluded that by restricting the flexing of the dislocations used in the calculations, a smaller yield strength would be predicted.

There is another contribution to the elastic interaction between a dislocation and solute atom; that which results from the difference in elastic properties of the solute atom and the matrix (22). If a solute atom has the same size as the solvent atom but has different elastic constants, there will be no lattice distortion, but there will be an interaction between the solute atom and dislocation. This interaction occurs because the strain energy associated with the dislocation will be altered as it moves near an elastically softer or harder spot in the matrix.

Fleischer (23) considered the flow stress to be influenced by both the differences in the size and differences in the modulus. Because the modulus difference should interact with screw dislocations as well as edge dislocations, it would be expected to be the dominant hardening factor. From a study on copper-base alloys, Fleischer (24) concluded that both size and modulus effects are substantial and that they contribute to increased strength in varying amounts depending on the solute

atom characteristics. Fleischer also stated that the strengthening effect attributed to electrical interactions (17,18) would not be present if the effect of the elastic modulus is considered. This implies that the solute valence influences the effective atomic modulus but is of no separate importance. Later an expression was derived (25) for the increase of the flow stress which predicted that it should be proportional to the square root of the concentration.

The bond energy model was first considered in connection with the thorium-carbon system by Peterson and Skaggs (26). The bond energy model was based on the formation of covalent bonds between an interstitial solute carbon atom and its six nearest neighbor thorium atoms. The lattice strain of a dislocation near a carbon atom in solution would change the length and orientation of these bonds and therefore their energy. This change could result in a dislocation-solute atom interaction.

Both the theories and experimental results indicate that in solution strengthened alloys the relative atomic size, the elastic and electrical properties of the solvent and solute atoms are significant variables in determining the flow stress of a solid solution.

The added strength of a solid solution alloy is due to obstacles, which a moving dislocation encounters as it passes through a metal crystal. The spacing L of these obstacles, along the dislocation length, is one of the parameters used

in both the Mott-Nabarro and Fleischer theories. Since the flow stress is a function of both the strength and the spacing of the obstacles, some choice of L must be made. The spacing L is strongly affected by the radius of curvature to which the dislocation can be bent by the applied stress. The bending of the dislocation is resisted by its line tension which tends to keep the length of a dislocation to a minimum. Under an applied stress τ the dislocation contacts obstacles and bows out between them to a radius of curvature r as given by $r = \Gamma/b\tau = \mu b/2\tau$, where Γ is the line tension, b is the Burgers vector, and μ is the shear modulus. From this restriction on the radius, it can readily be seen that for a concentrated solution the dislocation will be straight, as L is much smaller than $\mu b/2\tau$ and for very dilute solution L becomes larger allowing the dislocation to bow out more between the obstacles. If the interactions between the obstacles and the dislocation are weak the dislocation remains straight as the flow stress necessary to overcome the obstacles is small. In the case of a straight dislocation only those obstacles which lie in a nearly straight line are felt, resulting in a spacing such that $L \sim b/2c$ where c is the solute concentration. For stronger interaction, the applied stress is increased and the dislocation bows to a smaller radius of curvature. By bowing out between the obstacles the dislocation is more likely to come in contact with other obstacles and give a smaller spac-

ing with $L \sim b/\sqrt{2c}$. (25).

These theories are only approximate, but they indicate that the low temperature hardening should vary as $c^{1/2}$ for dilute solutions and as c in more concentrated solutions (27). Both types of dependence have been observed experimentally, with $c^{1/2}$ dependence more prevalent (25).

Precipitation Hardening

The basic requirement for obtaining a precipitation hardened alloy is that the quenched alloy be a supersaturated solid solution. Although this condition does not insure that the alloy will be capable of being hardened, it is a necessary requirement. As the excess solute precipitates, the material becomes harder. If the aging that causes the precipitation is allowed to continue, the size of the precipitated particles increases and the alloy becomes softer or overaged. The strengthening produced by the second phase particles is usually additive to the solid solution strengthening caused by the solute remaining in the matrix. For a complete understanding of the strengthening resulting from a second phase particle, many factors must be taken into account. These factors include the size, shape and distribution of the particles, the strength, ductility and strain-hardening behavior of the matrix and second phase, the crystallographic fit and the interfacial energy and bonding between the phases.

As a precipitate is formed from the solid solution, an additional obstacle to the movement of dislocations is created. With the precipitate particles lying in or cutting through the slip planes, the glissile dislocations may continue to move only by cutting through the particles or taking a path around the obstacles. The first dislocation theory on the strength of aged alloys was that of Mott and Nabarro (19, 28) which included solid solution strengthening. Mott and Nabarro considered the strengthening of an alloy to be due to the different atomic sizes (solute to solvent), causing internal stresses in the matrix. This same concept can be applied to groups of solute atoms in precipitation hardened alloys. The expression derived, using a rigid dislocation line, was independent of particle spacing and dependent only on the mismatch function and solute concentration. Mott (20) later introduced the idea of a curved dislocation in connection with Guinier-Preston zones.

The limiting radius to which a dislocation can bend under the influence of stress ($r = \mu b / 2\tau$) aids in explaining the effect of the precipitate spacing on the strengthening of an alloy. In the cases of overaging, the particles are much further apart than the limiting radius ($L \gg r$). Orowan (29) proposed an explanation for the decrease in flow stress of an overaged alloy, in which the dislocations under

an applied stress can "by-pass" the obstacle. The applied stress forces the dislocation to bow out into the region between the particles and this bowing out increases as the stress is increased. As the stress is increased, the dislocation is forced between the obstacles leaving them enclosed in a small dislocation ring. The yield stress is then the stress needed to bend the dislocation line into a radius of approximately $L/2$ i.e., $\tau = \mu b/L$. The yield stress thus varies inversely as the spacing between the precipitate particles and the alloy softens as it overages.

As the spacing between the particle is reduced, a point is reached below which it is easier for the dislocation to cut through the particles than to bow out around them. There may also be a range of spacings in which cross slip can help avoid cutting through the particles. If the total volume of the precipitate is assumed to be constant, small particle size means short distance between the precipitated particles. Using this assumption, Nabarro (30) predicted a relationship between yield stress and the distance between the particles L of $\tau = \text{const.}/L$ which is valid for small values of L . This indicates that the stress increases as L increases. Thus, this relationship and $\tau = \mu b/L$, from above, indicate that

there is a transition, between the two regions, where a maximum occurs in the stress vs L curve, which corresponds to the "critical particle size". This "critical particle size" is reached when the spacing L is such that it is equally probable for the dislocation to cut through the particles or pass between them. It should be noted, that when the precipitate ceases to be coherent and its crystal structure is different from that of the matrix, the particle can no longer be sheared by the dislocations. The factors governing the particle's resistance to shear and a comparison of theoretical calculation with experimental results has been compiled by McLean (21) and Honeycombe (31).

The strength of alloys which are hardened by a precipitate is usually not considered to be sensitive to temperature. The reason for this is that the precipitate particles are generally large enough (long range barriers) so that thermal activation cannot assist dislocations in cutting through them. The flow stress of an Al-Ag alloy (32), treated to contain particles $100 \text{ \AA}$ in diameter, was not affected by temperature. But, if the particles are very thin, a temperature dependence can be expected. In the Al-Cu system (33), the particles which form at the start of aging consist of platelets of copper one atom thick. Here the barrier, if it cuts across the slip plane, is a short-range obstacle which temperature fluctuations can help the dislocation overcome. The activa-

tion energy and activation volume can be determined in a precipitation hardened alloy by temperature and strain rate changes during tensile testing, if the alloy exhibits a temperature dependent flow stress. Byrne et al. (34) did this on Al-1.7 a/o Cu and concluded that the obstacles, which are overcome through the help of thermal fluctuations, were due to precipitate particles and not to obstacles produced by strain.

Thorium, a face-centered cubic metal, and the first element in the actinide series of rare-earths, is of interest and importance from both a fundamental as well as a practical standpoint. It exhibits a yield point which is not normally observed in face-centered cubic metals. Thorium has a strong temperature dependence of the flow stress, which is usually associated with the body-centered cubic metals. Also, thorium appears to be different from the other face centered cubic metals in that it has a large solid solubility of carbon (35), 0.35 w/o at room temperature, and a nitrogen solubility of about 0.05 w/o at 845°C (36). In view of these characteristics, Peterson and Skaggs (26) studied thorium-carbon alloys containing from 0.008 to 2.83 a/o carbon, over a temperature range of 4.2° to 573°K and at various strain rates. The flow stress of the thorium-carbon alloys was made up of a thermally activated component and an athermal component. The increase in the flow stress was found to vary linearly with carbon

concentration. It was therefore believed that a systematic study of the effect of nitrogen content, temperature and strain rate on the flow stress and yield point behavior of thorium would contribute to a better understanding of the mechanism of interstitial solid solute hardening.

In a more practical vein, thorium has a potential role as a fuel element component in nuclear reactors. When exposed to a neutron flux, it is capable of being transmuted to U^{233} , which is fissionable. However, pure thorium has a low tensile strength and a high creep rate at elevated temperatures. Consequently, there is a need to develop new thorium alloys which meet the physical, chemical and nuclear requirements of a nuclear fuel material. In this light, a comprehensive study of the effect that nitrogen has on the strength of thorium should be useful.

EXPERIMENTAL PROCEDURE

Specimen Preparation

A thorium billet, prepared by the magnesium intermediate alloy process described by Peterson et al. (37), was used to prepare all the specimens tested in this investigation. This single material source was utilized in order to eliminate composition variations except in the nitrogen content. The chemical analysis of this billet is given in Table 1. The billet was cold rolled to a 3/8 inch thick plate and five 150 gram portions for test specimens were sheared off, plus a 30 gram piece, which was used to prepare a thorium-nitrogen master alloy. The thorium-nitrogen master alloy was prepared by arc-melting the base alloy in a predetermined volume of nitrogen gas. Portions were then arc-melted with the appropriate amount of master alloy to obtain 100, 200, 350 and 600 wt ppm nitrogen alloys. These alloys were arc-melted and turned three times to obtain a uniform nitrogen distribution. The base metal sample and the thorium-nitrogen alloys were then remelted into a "finger" mold (3/4 inch diameter by 6 inches) and cold swaged into 1/4 inch diameter rods.

Specimens used in the constant stress or creep tests were machined from the as-swaged 1/4 inch rods. These specimens were 2 1/2 inches long with a reduced section which was 0.230 ± 0.001 inches in diameter by 1.5 inches long. Tensile specimens were prepared by swaging the 1/4 inch diameter rods to a

Table 1. Analysis of thorium billet BEB-1-115

Element	Content, wt. ppm	Element	Content, wt. ppm
O	130	Ni	<20
N	20	Ta	100
C	<10	Ti	N.D. ^a
Fe	20	W	35
Al	<20	Y	N.D.
Ca	<20	Co	N.D.
Cr	<20	Cu	N.D.
Mn	<20	Mg	<20
Si	<20		

^aN.D., not detected.

0.097 inch diameter and cutting into 2 inch lengths. Each piece was cleaned in a hot nitric acid-sodium fluosilicate solution to remove oil and the oxide surface layer. The ends of the specimens were masked off so that a one inch gage length could be electropolished to a reduced diameter of 0.090 ± 0.001 inches. Electropolishing was accomplished at a D.C. potential of fifty volts in a 6 per cent perchloric acid in methyl alcohol solution which was maintained at -70°C .

A recrystallization and recovery study was conducted to determine the annealing time and temperature at which strain free equiaxed grains would be obtained. It was found that an annealing time of one hour at 800°C for the base metal and the 100 ppm and 200 ppm nitrogen alloys and one hour at 1000°C for the 350 ppm and 600 ppm nitrogen alloys would produce equiaxed recrystallized grains with a grain size of approximately 1500 grains per square millimeter. Alloys containing 350 and 600 ppm nitrogen were above the solubility limit and required a

cold water quench from 1000°C to retain the nitrogen in solution. Annealing was done under a dynamic vacuum so that any hydrogen in the specimens would be evolved as shown by Peterson and Westlake (38).

After the specimens were prepared, a sample from each alloy composition was analyzed for carbon, nitrogen and oxygen. The average results of these analyses are given in Table 2.

Table 2. Analysis of thorium-carbon alloy specimens after fabrication and annealing

Nitrogen content ^a		Carbon	Oxygen
0.04 a/o	23 wt ppm	4 wt ppm	239 wt ppm
0.16	97	55	245
0.32	193	48	300
0.58	348	51	256
0.97	593	57	240

^aAverage of a minimum of five chemical analyses.

Constant Strain Rate Measurements

The constant strain rate measurements and relaxation experiments were run on a screw-driven Riehle Model FS-10 Universal Screw Power Testing Machine. The cross-head speed was found to differ from the value indicated on the selection dial and the instrument was recalibrated. The actual cross-head speed was used in the calculations made in this investigation. The load was calibrated and found accurate to within ± 1 per cent.

Tensile tests were made with the specimens maintained at a constant temperature by various constant temperature baths or furnaces. A compression tube was fastened to the underside of the lower moveable cross-head through which a pull rod was extended down from the upper fixed cross-head. The specimens were attached to the pull rod and compression tube by serrated four jaw collets.

Below room temperature, constant temperature freezing and boiling media were used (i.e., liquid nitrogen, ice water, etc.). The temperature of the specimen was controlled by placing the compression tube within a Dewar flask and maintaining the liquid level above the specimen. Modification of the compression tube was necessary for testing in liquid helium. An elongated, thin walled stainless steel tube was used to reduce the heat transfer through the tube to minimize helium boil off.

A silicon oil bath heated by an immersion heating coil was used for the temperature range of 60°C to 200°C. At temperatures above 200°C, the compression tube was wrapped in heating tape or contained in a cylindrical resistance furnace. Because thorium oxidizes readily at these higher temperatures, an argon gas atmosphere was maintained around the sample under a slight positive gage pressure. Two thermocouples, one near the top and one near the bottom of the specimen, were used to measure the temperature which was held to within less than 1°C

during the course of the run. Oxidation of the specimens was found to be negligible.

Since the tensile specimens were completely enclosed in the apparatus used to control the temperature, it was necessary to measure the elongation indirectly by measuring the motion of the lower cross-head with a Riehle Model DC Deflectometer. The deflectometer actuated a linear differential transformer which sends an electrical signal to a recorder. This recorder traces the load as a function of lower cross-head motion. The true stress-true strain curves were determined from these traces by taking into account the elastic contribution of the tensile apparatus.

The specimens were tested using a strain rate change technique. The cross-head speed was changed cyclically through four different speeds corresponding to strain rates of 5.2×10^{-5} , 2×10^{-4} , 8×10^{-4} and 1.44×10^{-3} per second during each test. Strain rate changes were made at intervals of 0.01 to 0.05 inches elongation. The load-elongation trace for a given strain rate was not continuous, and it was necessary to interpolate in order to construct complete true stress-true strain curves at constant strain rate. This method of interpolating was justified by the fact that strain rate changes did not measurably change the work-hardening characteristics and that the changes in flow stress with strain rate were reversible below 250°C.

Stress relaxation tests were run at 120°C and 200°C to measure the athermal component of flow stress directly. This test consisted of stopping the cross-head motion at several intervals during the tensile test and observing the decrease in load as a function of time. After a period of time, a constant load was reached. The bath temperature was maintained to within $\pm 0.1^\circ\text{C}$ of the nominal temperature during these tests. Stress relaxation tests were also run over the temperature range of 250°C through 400°C, but variations in the temperature of $\pm 1^\circ\text{C}$ introduced larger errors in the constant load value.

Constant Stress Measurements

It is desirable, in an investigation of this type, to explore a range of strain rates for which the ratio of maximum to minimum strain rate is as large as possible. In order to extend the measurement of flow stress to strain rates below those obtained with the tensile machine, it was necessary to use a constant stress or "creep" test. This was accomplished with a balanced lever arm, dead weight loading system. The two machines used for this measurement had a 20 to 1 and a 5 to 1 lever arm ratio. Each machine had a modified load unit that was devised to facilitate immersion of the specimen in a constant temperature bath. This modification consisted of a compression load tube which extended below the rigid cross-head of the creep machine similar to that used in the

constant strain-rate test. The measurement of the strain of the specimen was made with precision bonded strain gages, type EA-06-500BH-120 manufactured by Micro-Measurements Division, Vishay Intertechnology, Inc., Romulus, Michigan. The strain indicator used a Wheatstone Bridge circuit, with a readout in micro-inches per inch strain.

The active gage was bonded to the thorium creep specimen and measured the strain in the specimen. A compensator gage and dummy specimen were placed in close proximity to the specimen under load and served to balance out changes due to temperature variations.

In order for a strain gage of this type to measure strain accurately, the bond between the surface of the test specimen and the strain gage must be of a very high quality. The procedure used in attaching the strain gages using Eastman 910 adhesive was as follows:

After cleaning with acetone, the surface of the specimen was mechanically polished down to bright metal with 500 grit abrasive cloth, cleaned with acetone and then the surface was neutralized with Budd GC-4 Neutralizer which is a proprietary product believed to be a dilute solution of ammonia, with a small amount of detergent added. The surface was cleaned with Bond-Fix, manufactured by Tri-R Chemicals, Inc. which activates the surface for faster and better bonding. The gage was picked up on a piece of cellophane tape and Bond-Fix was

applied to the back of the gage and allowed to dry. Care was taken not to allow the tape adhesive to be dissolved, and carried over on to the gage back. The gage was located over the specimen and one edge of the tape was attached to the specimen to hold it in alignment. While holding the free edge of the tape and gage away from the surface of the specimen, a continuous bead of Eastman 910 adhesive was drawn into the fillet formed between the edge of the gage and the specimen surface. Care was taken not to allow the applicator to apply pressure to the cement film as hardening of the cement is induced by pressure. The gage and tape was then wiped down with a firm, progressive pressure causing the cement to flow out into a thin film under the gage. The pressure was maintained a minimum of one minute before peeling off the tape. A thin layer of waterproofing was applied to the gage and allowed to dry. The lead wires were secured to the specimen with tape to prevent damage to the gage. The lead wires were then soldered to the gage tabs and waterproofing applied over the entire reduced gage length of the specimen.

Thorium undergoes anelastic deformation on loading and unloading which must be taken into account at the start of each creep test. It was possible to eliminate this anelastic effect by applying a load which gave a stress just below the predicted athermal stress component. This load was allowed to remain for a period of 24 hours at which time the stress

was increased to obtain a strain rate of approximately 10^{-8} per sec. The stress was allowed to remain at this level until a constant strain rate was obtained. The stress was reduced in steps of several hundred psi and the strain rate recorded at each step. The procedure was continued until a stress was reached at which no additional strain was observed during a 60 hour period resulting in a strain rate of 10^{-12} per second. This stress was defined as being the athermal stress component. Once the athermal stress component had been measured, the stress was increased incrementally and the resulting strain rates recorded. In determining the strain rates, a minimum strain of 10×10^{-6} was measured. Strain rates as high as 10^{-5} per second, which is the lower range obtained in the tensile test, were measurable. It was then possible to combine the creep and tensile data to construct a flow stress-strain rate relation over a strain rate range of 10^{-12} to 10^{-3} per second at a given temperature and strain.

Two specimens of each alloy were tested at 0°C in an ice water bath and at 60°C in a silicone oil bath. The temperature in the silicone oil bath was controlled by a thermostat to $\pm 0.1^{\circ}\text{C}$. These specimens were prestrained at room temperature in a tensile machine of approximately 1 per cent strain. A total strain of $1000-3000 \times 10^{-6}$ was required to complete a creep test. In many cases it was desirable to recheck the data obtained from a given specimen. Since the work-hardening for these thorium alloys was small, it was possible to repeat the

creep test on a particular specimen and reproduce the entire flow stress-strain rate curve to within several hundred psi.

Transmission Electron Microscopy

A transmission electron microscopy study of the aged thorium-nitrogen alloys was undertaken to obtain information on the size and shape of the precipitate particles. The technique used for thinning the thorium foils was basically that described by Despres (39). The technique essentially consisted of electropolishing a 0.003 to 0.006 inch thick thorium specimen sandwiched between two Inconel washers to the thickness required for electron transmission studies. The thorium metal foil was cut into 0.125 inch disks by a small punch. These disks were placed between two Inconel washers, I.D. = 0.065 in., O.D. = 0.125 in. and 0.007 in. thick and the washers were spot welded together at two diametrically opposite points at the outer edge of the washers.

The specimen was thinned by electropolishing in a 5 per cent perchloric acid-methyl alcohol solution maintained at -70°C in a dry ice-methyl alcohol bath. Two pointed cathodes, insulated with lacquer except for the tips were positioned about 1/8 inch apart with the specimen centered between them.

A voltage of 3 to 10 volts was applied between the cathodes and the specimen as required to maintain good electropolishing conditions and a specular thorium surface. The thinning process was continually watched by means of a low magnifica-

tion microscope viewing through the glass container. A light source behind the specimen was used to aid in detecting the moment when a hole first appeared in the specimen. The time required for the thinning operation varied from 15 to 40 min. When a hole was detected, the specimen was removed from the electrolyte and washed in a -70°C methyl alcohol bath for approximately 15 minutes and then in another methyl alcohol bath at room temperature. The washer and specimen assembly were dried and placed directly into the sample holder of the electron microscope.

The high density of thorium required a very thin specimen for transmission electron microscopy work. Incorporation of the washer as a supporting frame eliminated most of the mechanical handling problems associated with very thin foils. The washers and thinned specimens could be inserted into the electron microscope holder without any modification of the microscope holder. The major handling problem occurred during the cutting of the disk and mounting it between the washers. Care was necessary during these operations to avoid distortion of the specimen.

RESULTS

Specimen Characterization

At the beginning of this research project the annealing characteristics of the thorium-nitrogen alloys were studied. It was found that the addition of nitrogen to thorium increased the recrystallization temperature, but did not measurably refine the grain size. Small specimens, one of each alloy, were annealed one hour at temperature and furnace cooled. The specimens were metallographically examined and the diamond pyramid hardness measured. Uniform equiaxed grains were first observed in the base alloy, 0.16 a/o and 0.32 a/o nitrogen alloys at 700°C, 750°C and 750°C, respectively. The 0.58 a/o and 0.97 a/o nitrogen alloys did not recrystallize completely until annealed at 800°C and 850°C respectively. The diamond pyramid hardness-annealing temperature curves for the base alloy, 0.16 a/o and 0.32 a/o nitrogen are shown in Figure 1. Data for alloys containing 0.58 and 0.97 a/o nitrogen were not included as it was essentially the same as the 0.32 a/o nitrogen when annealed and furnace cooled. The diamond pyramid hardness measurement revealed that the hardness increased with increasing nitrogen content up to 0.32 a/o nitrogen. Above 0.32 a/o nitrogen the hardness did not increase with increasing nitrogen concentration, but remained constant, indicating that these alloys were above the nitrogen solubility limit. Metallographic examination of the 0.97 a/o

Figure 1. Room temperature diamond pyramid hardness after one hour anneal at temperature

nitrogen alloy, annealed at 850°C for one hour and furnace cooled, revealed thorium-nitride precipitate particles throughout the matrix. After annealing at 1000°C for one hour and quenching into cold water, no evidence of thorium nitride precipitate particles was detected in this alloy.

In order to determine the effect of the cooling rate on the strength of the thorium-nitrogen alloys, a set of tensile and hardness specimens were held at 1000°C for one hour and quenched into cold water. These quenched specimens exhibited an increase in hardness and flow stress with increasing nitrogen content throughout the composition range. The quench had a negligible effect on the hardness and flow stress of the nitrogen alloys below the solubility limit but increased the hardness and strength of alloys containing 0.58 and 0.97 a/o nitrogen. Figure 2 shows the hardness-composition data of the furnace cooled and quenched alloys.

Due to difficulty in obtaining consistent analytical results for the 0.58 a/o nitrogen alloy and as a check on the amount of nitrogen retained in solution by quenching, resistance ratio measurements were made on the five thorium-nitrogen alloys. A resistivity value of 15.80 $\mu\Omega$ cm at 300°K for pure thorium (40) was used to calculate the resistivity at 4.2°K. from the resistance ratio. The result indicated that the residual resistivity is directly proportional to the nitrogen concentration with a slope of 3.7×10^{-3} $\mu\Omega$ cm/ppm nitrogen. Several different specimens of each alloy were used in deter-

Figure 2. Room temperature diamond pyramid hardness of thorium as a function of nitrogen content after various heat treatments

mining this linear relationship. The results were consistent and in agreement with the chemical analysis. The residual resistivity of the quenched alloys, shown in Figure 3, indicated that the nitrogen was retained in solid solution.

The lattice parameter values for the five thorium-nitrogen alloys are shown in Figure 4. It was found that the lattice parameter increased linearly with increasing nitrogen content. The specific increase in the lattice parameter with nitrogen content, $1/a_0 da_0/dc$, was calculated to be 0.067, where the nitrogen concentration is in atom fraction.

The effect of grain size on the strength was determined by preparing a series of coarse grained tensile specimens. After annealing at 1000°C for 3 to 72 hours, the tensile specimens had a grain size of from 150 g/mm² to 960 g/mm². The 2 per cent offset flow stress of the coarse grained specimens varied from -10 to +8 per cent of the corresponding fine grained specimens. It was concluded that the contribution of grain boundaries to the strength is quite small.

The majority of the stress-strain curves obtained for the thorium-nitrogen alloy were smooth and showed no evidence of a yield point phenomena. However, a small upper and lower yield point was observed in a few of these alloys which is in contrast to the larger yield point found in the thorium-carbon alloys (26).

Figure 3. Resistivity at 4.2°K as a function of nitrogen content

Figure 4. Lattice constants of thorium-nitrogen alloys

Solid Solution Alloys

The flow stress of thorium was found to be dependent on temperature, nitrogen content, strain and strain rate. Figure 5 shows the flow stress at 1 per cent plastic strain as a function of temperature. The flow stress-temperature curve shows that the flow stress for the three lowest nitrogen alloys decreased linearly with temperature from 4.2°K to 300°K and then asymptotically approaches a nearly temperature independent value at about 473°K. The flow stress for these alloys is essentially independent of temperature between 473°K and 673°K and then above 673°K it is again temperature dependent. The reoccurrence of the temperature dependence above 673°K is due to recovery processes taking place during the tensile test.

Alloys containing 0.58 and 0.97 a/o nitrogen deviated from the above behavior at both the high and low ends of the temperature range. At 77° and 4.2°K, the flow stress of these high nitrogen alloys deviated from the linear temperature dependence observed for the lower nitrogen alloys. To indicate the amount that these alloys deviated from a linear temperature dependent, the flow stress has been extrapolated by a dashed line, from 198°K to 0°K. It should be noted, that even though the flow stress deviated from a linear relationship, there is still a significant increase in flow stress from 198°K to 4.2°K. Above 523°K the flow stress of the two

Figure 5. Flow stress at 1 per cent plastic strain versus temperature for the solid solution thorium-nitrogen alloys

alloys above the solubility limit increased to a maximum at about 623°K and then decreased to a value approaching the temperature independent flow stress of the lower nitrogen alloys. Tensile tests at 523°K and 573°K revealed that after a relaxation of ten minutes or more an increase in the flow stress resulted when deformation was continued. This increase in flow stress indicated that an aging process was taking place. Both the high and low temperature phenomena will be discussed later in more detail.

This flow stress-temperature behavior of the thorium-nitrogen alloys is similar to that which has been obtained by other investigators studying thorium and thorium alloys (26, 41,42). These studies found that the flow stress appeared to be divided into a thermally activated component and athermal component. It will be assumed that the flow stress, σ is a sum of a thermal component, σ^* , and an athermal component σ_μ . The dashed line in Figure 5, which is an extension of the flow stress in the temperature-independent region where $d\sigma_\mu/dT = (\sigma_\mu/\mu)(d\mu/dT)$ (4), represents the athermal component of the flow stress. It is assumed that the change in σ_μ with temperature is due to the change in the shear modulus with temperature. This slope, $(\sigma_\mu/\mu)(d\mu/dT)$, was estimated to be 2.4 psi/°K from the elastic constants for thorium reported by Armstrong et al. (43).

Relaxation experiments were used to measure the athermal

component directly at 393°K and 473°K. The cross head movement was stopped at several intervals during the tensile test and the load was allowed to decrease until a constant load was reached. The time necessary to reach a constant load increased with increasing nitrogen content and decreasing temperature. These constant load values on the load-elongation plots were connected together forming a continuous athermal load-elongation curve. By using this technique, the athermal component could be obtained at any strain at these temperatures.

The athermal stress component was also measured directly by constant stress measurements or "creep test" at 273°K and 333°K. The athermal component was found by decreasing the load on the specimens until a stress was reached below which plastic strain was not observed. The results from these tests showed that the athermal stress component was independent of the nitrogen content and temperature. For a given strain, the athermal stress component measured at 273°K and 333°K by the constant load technique, at 393°K and 473°K by the relaxation technique, and the temperature independent flow stress at 573°K were all equal to within the accuracy of the measurements. The athermal component of the Th-0.97 a/o nitrogen alloy was generally somewhat higher than the other alloy. This could have been due to the high degree of supersaturation and possible aging effects after quenching. The values of

the athermal stress at 1 per cent strain obtained by the different methods are shown in Table 3.

The thermally activated component of the flow stress at any given temperature and strain was obtained by the expression $\sigma^* = \sigma - \sigma_{\mu}$. The shear stress in face centered polycrystals can be related to the observed tensile stress by a factor of 3.1 as shown by

$$\tau^* = \frac{\sigma - \sigma_{\mu}}{3.1} \quad (5)$$

where τ^* is the thermal component of the effective shear stress. The thermal flow stress component was found to increase linearly with nitrogen over a temperature range 198°K to 333°K as shown in Figure 6. Figure 7 shows the effect of nitrogen on the thermal shear stress component at 77°K and 4.2°K. Here the thermal shear stress varies with the square root of the solute concentration. The change from a linear dependency to a square root dependency of the flow stress on nitrogen concentration caused the flow stress of the alloys containing 0.58 a/o and 0.97 a/o nitrogen to deviate from the linear temperature dependency at 77°K and 4.2°K. The three lowest nitrogen alloys had a small enough nitrogen content so that this change from C to $C^{1/2}$ dependent was not noticeable in the flow stress-temperature relationship.

Generally, the effect of decreasing temperature on the stress-strain behavior of face centered cubic metals is to increase the work hardening rate at the lower temperatures.

Table 3. Observed values of the athermal stress component of flow stress at 1 per cent strain

Nitrogen content a/o	Temperature					Average
	273°K	333°K	393°K	473°K	573°K	
0.04	6800 psi	7800 psi	5900 psi	6000 psi	7000 psi	6700psi
0.16	8600	7000	7000	6300	7900	7400
0.32	8900	7700	6600	6900	8000	7600
0.58	7800	6900	7000	6800	--	7100
0.97	10900	8200	8800	9200	--	9300

Figure 6. Thermal shear stress as a function of nitrogen content at various temperatures

Figure 7. Thermal shear stress as a function of nitrogen content at 4.2°K and 77°K

Thorium does not behave in this manner as the work hardening rate does not increase as much as usually attributed to face centered cubic metals. It was found that the initial rate of work hardening for these thorium-nitrogen alloys was not a function of the temperature of deformation or of the nitrogen content. The stress-strain behavior of these thorium-nitrogen alloys can be seen in Figures 8 through 12.

The thermally activated component of flow stress gives rise to a relationship between the flow stress and strain rate. A typical plot of the variation of flow stress with strain rate is given in Figure 13. The slope of the plot of flow stress versus log strain rate, $\Delta\sigma/\Delta\ln\dot{\epsilon}$, is called the strain rate parameter and in this study was nearly constant over a range about 10^{-8} to 10^{-3} per second strain rate. Data from the constant stress measurements were combined with the results from tensile tests at various strain rates to construct semilog plots of flow stress versus strain rate over a range of 10^{-12} to 10^{-3} per second strain rate. Constant stress measurements were made for each alloy at 273°K and 333°K for specimens prestrained 1 per cent. The constant stress measurements were also made on specimens prestrained 7 per cent to determine the effect of strain on the strain rate parameter. It was found that the strain rate parameter did not change with strain. The strain rate parameter was also determined from tensile test results for a larger range of temperature, 4.2°K to 823°K, but over a smaller strain rate

Figure 8. True stress vs. true strain for thorium-0.04 a/o nitrogen at various temperatures

Figure 9. True stress vs. true strain for thorium-0.16 a/o nitrogen at various temperatures

Figure 10. True stress vs. true strain for thorium-0.32 a/o nitrogen at various temperatures

Figure 11. True stress vs. true strain for thorium-0.58 a/o nitrogen at various temperatures

Figure 12. True stress vs. true strain for thorium-0.97 a/o nitrogen at various temperatures

Figure 13. Flow stress of thorium-0.58 a/o nitrogen alloy versus strain rate at 1 per cent prestrain and 273°K

range, 10^{-5} to 10^{-3} per second. This study revealed that the strain rate parameter was constant with strain and strain rate and was a function of nitrogen content and temperature. The strain rate parameter increased nearly linearly with nitrogen content at temperatures between 198°K and 473°K. At 77°K the strain rate parameter deviated from this linear relationship and was proportional to the square root of the nitrogen concentration. Figure 14 is a plot of the strain rate parameter versus nitrogen content at 77°K, 198°K and 473°K. The curvature of the 77°K data indicates a square root dependent on nitrogen content. Figure 15 shows the variation of the strain rate parameter with temperature for the thorium-nitrogen alloys. The error brackets at 77°K and 473°K indicate the variation from three or more tests, while the error brackets shown for the 0.32 a/o nitrogen alloy, represent the estimated error limits. This parameter goes through a maximum at 273°K, with the three alloys below the solubility limit reaching a very small value between 523°K and 623°K. The strain rate parameter for the alloys above the solubility limit increased again to a second maximum at 623°K. This second maximum is associated with the aging phenomenon noted earlier in connection with the maximum in the flow stress-temperature curve. Above 623°K the strain rate parameter starts to increase again for the three lower nitrogen alloys as high temperature deformation mechanisms become active.

2

Figure 14. Variation of the strain rate parameter with nitrogen content

Figure 15. Variation of strain rate parameter with temperature for thorium-nitrogen alloys

The variation of the activation volume with temperature and nitrogen content is shown in Figure 16. The activation volumes were nearly independent of temperature over the temperature range from 77°K to 300°K and then increased rapidly at higher temperatures. The activation volumes, in the temperature independent region varied from $19b^3$ to $80b^3$ and decreased with increasing nitrogen content. The activation volumes for face centered cubic metals are generally much higher, $100b^3$ to $1000b^3$, while those for body centered cubic metals are of the order of $5b^3$ to $100b^3$.

The activation energy was calculated from the experimental data by employing the expression (4)

$$\Delta H = kT^2 \left(\frac{\Delta \sigma^*}{\Delta T} \right)_{\epsilon, \epsilon} \left(\frac{\Delta \ln \epsilon}{\Delta \sigma} \right)_{\epsilon, T} \quad (6)$$

The parameter, $\Delta \sigma^*/\Delta T$, was taken from the slope of the best straight lines from Figure 5 (σ vs. T) between 0°K and 333°K. The activation energies were calculated for each alloy in this temperature range and these values are shown in Figure 17. The curve was drawn through the average values and the estimated error limits are shown by the error brackets. A best straight line drawn through the data points and extrapolated to the temperature at which $\tau - \tau_u = 0$, T_c gives a value of approximately 1.2 eV for the maximum interaction energy. The effect of nitrogen on the activation energy was smaller than the experimental uncertainty.

Figure 16. Activation volume vs. temperature for thorium-nitrogen alloys

Figure 17. Activation energy for plastic deformation vs. temperature

At 4.2°K the flow stress-strain curves for these thorium-nitrogen alloys were serrated. These serrations were accompanied by audible sounds and the number of serrations per unit strain increased with strain and strain rate. The base alloy did not show this discontinuous deformation but it was very prominent in alloys containing 0.58 and 0.97 a/o nitrogen. The drop in load associated with these serrations increased with strain and nitrogen content. Similar serrations were observed by Zabel (42) in thorium-zirconium alloys tested at 4.2°K. Discontinuous deformation at 4.2°K has been observed in aluminum (34,44,45) and at 20°K in stainless steels (46). Serrations of this type in the plastic region have been studied extensively by Basinski (47) who attributed the behavior to local adiabatic heating due to the energy released during plastic deformation. Localized heating would decrease the flow stress in a small region to less than that at the test temperature. The result is a sudden increase in plastic strain and a decrease in load. A metal with a large temperature dependence of the flow stress such as thorium should show this discontinuous deformation at very low temperatures more than a metal with a small temperature dependence.

Precipitation Hardened Alloys

It was reported in the preceding section that the strain rate sensitivity and flow stress of alloys containing 0.58 and 0.97 a/o nitrogen decreased to a minimum between 473°K

and 523°K but increased again to a maximum at about 623°K. An investigation was conducted on these alloys to establish the characteristics of this phenomenon. It was found that for specimens aged for two hours at various temperatures there was a maximum in the room temperature hardness after aging at 573°K. The aging time and temperature which produced the maximum hardness was determined by holding the quenched alloys at temperatures ranging from 548°K to 673°K, for times ranging from 15 minutes to 25 hours. Room temperature hardness curves for both alloys are shown in Figure 18. These curves indicate that an aging time of 16 hours at 573°K was required to obtain the maximum hardness in both alloys. At 673°K, overaging resulted even for aging times as short as 20 minutes.

Tensile specimens aged at 573°K for 16 hours were tested using the same technique as that used for the unaged alloys in obtaining the constant strain rate measurements. True stress-true strain curves at a number of temperatures are shown in Figures 19 and 20. It was found that there was no measurable change in the work hardening characteristics of the aged alloys from that of the unaged alloys. Elongation to necking decreased upon aging due to the fact that the flow stress increased but the work hardening rate did not increase proportionally. Table 4 gives the flow stress at 1 per cent strain for the alloys containing 0.58 and 0.97 a/o nitrogen in the aged and unaged conditions.

Figure 18. Variation of the diamond pyramid hardness with time at various temperatures

Figure 19. True stress vs. true strain of the precipitation hardened thorium-0.58 a/o nitrogen alloys at various temperatures

Figure 20. True stress vs. true strain of the precipitation hardened thorium-0.97 a/o nitrogen alloys at various temperatures.

Table 4. Comparison of the flow stress at 1 per cent strain of aged to unaged thorium-nitrogen alloys

Temp. °K	Unaged		Aged	
	0.58 a/o N	0.97 a/o N	0.58 a/o N	0.97 a/o N
77	39000	47700	43600	65700
198	30700	41300	33800	57200
273	20500	27600	28700	45500
296	16400	23000	27000	44900
333	14600	19500	24100	39400
396	9600	13400	22500	37800
473	8100	10900	17900	33100
523	9400	13100	19200	31100
573	12600	18600	15400	27300
623	14900	21600	12500	19600

The flow stress versus temperature curves shown in Figure 21 can be divided into four regions marked by changes in the slope of the curves. A change in the slope of a flow stress-temperature curve indicates a change in the thermally activated deformation mechanism. There is also a correlation between these four regions and the maxima and minima in the strain rate parameter and activation volume versus temperature curves shown in Figures 22 and 23. The region between 4.2°K and 333°K in Figure 21 shows that the flow stress varies linearly with temperature and that the slopes are similar to the unaged thorium alloys containing 0.32 a/o and 0.58 a/o nitrogen. The strain rate parameter values obtained in this temperature region for the aged alloys indicates also that the nitrogen remaining in solution is about 0.32 a/o and 0.58 a/o nitrogen. This is in agreement with the results obtained from the resistivity measurements on these aged alloys. Based on

Figure 21. Flow stress at 1 per cent plastic strain vs. temperature for the precipitation hardened thorium-nitrogen alloys

Figure 22. Variation of the strain rate parameter with temperature for the precipitation hardened thorium-nitrogen alloys

Figure 23. Activation volume vs. temperature for the precipitation hardened thorium-nitrogen alloys

these findings it was concluded that the temperature dependence of the flow stress in this region was due to the residual nitrogen in solution.

At 333°K the slope of both flow stress-temperature curves decreased sharply. This is the same temperature region in which the dissolved nitrogen contribution to the temperature dependence of flow stress for the unaged alloys decreased. This region is believed to be a transition region in which the thermal component of flow stress due to nitrogen in solution is disappearing as T_c is approached and a different thermal barrier, that due to the precipitation particles resulting from the aging becomes active. This interpretation of this region is reinforced by the sharp maximum in the activation volume-temperature curves.

The second peak in the strain rate parameter-temperature curves occurred between 523°K and 623°K and is associated with the structure produced by aging. This increase in the strain rate sensitivity was accompanied by an increase in the temperature dependence of the flow stress, and a constant activation volume over the same temperature range. It was assumed that this thermal component of flow stress is due to the thorium nitride precipitate particles.

Above 623°K, it is known from previous experimental results that overaging of the thorium nitride precipitate takes place and that high temperature deformation mechanisms are active. This is verified by the slight decrease in the slopes

of the flow stress-temperature curves and an increase in the activation volume.

Transmission electron microscopy was used to measure the size and shape of the precipitate particles. Foils of the 0.97 a/o nitrogen alloy in the quenched condition were aged for various times and temperatures. The specimens were then electropolished to a thickness suitable for observation in the electron microscope. Specimens aged at 400°C for times ranging from 1/2 hours to 4 hours had precipitate particles of 100Å to 550Å in size. Specimens aged at 350°C had particle sizes from 50Å to 430Å when aged 4 to 31 hours. It was found that the particle size increased with increasing aging temperature and time. When specimens were aged at 573°K (300°C) to produce the maximum hardness, no particles were observed even when aged for as long as 49 hours and examined at 190,000X. Figure 24 shows thorium nitride particles in samples which were aged at 400°C. Since the photomicrographs from which the particle sizes were determined are two dimensional projections of a three dimensional solid, it was not possible to determine the distance between particles. Two distinct size groups of particles were found in each specimen in which precipitate particles were detected. The larger size particles could have been due to heterogeneous nucleation of these particles, allowing a longer time for growth. From this investigation, it was concluded that the thorium nitride particles for optimum hardness were less than 36Å, 10 atomic diameters, in size

a

b

Figure 24. Electron transmission micrographs of thorium-0.97 a/o N, cold water quenched from 1000°C. (a) Aged at 400°C for 2 hr. (b) Aged at 400°C for 4 hr.

and were cubic in shape.

Below 523°K, it was assumed that the thorium nitride particles presented an athermal barrier to dislocation movement. This reasoning is indicated on Figure 21 by the dash lines representing an athermal component of flow stress for the two aged alloys. The values of the athermal component of flow stress were used to obtain the thermal components for the aged alloys in the temperature range 0°K to 333°K. These thermal components were equal, within the limits of the measurement, to the thermal component of the unaged alloys containing 0.32 a/o and 0.58 a/o nitrogen.

The activation volume and activation energies for the aged alloys were calculated for the temperature ranges, 0°K-333°K and 523°K-623°K. The values obtained in the lower temperature region were about the same as those obtained for the unaged alloys. Between 523°K and 623°K the activation volumes as shown in Figure 23 were $125b^3$ and $65b^3$ for the 0.58 a/o and 0.97 a/o nitrogen alloys respectively. These values would indicate that the size of the thorium nitride particles and the distance between them were quite small, as also indicated by the transmission electron microscopy study. In this temperature range, 523°K to 623°K, a value of 3eV was obtained for the activation energy for deformation associated with the precipitate particle. The activation energies for the aged alloys are given in Table 5.

Table 5. Activation energies for the aged thorium-nitrogen alloys

Temperature °K	Nitrogen content	
	0.58 a/o	0.97 a/o
77	0.13 eV	0.10 eV
198	0.37	0.39
273	0.57	0.73
294	0.71	0.82
333	1.14	1.25
523	2.4	2.6
573	2.5	2.7
623	2.6	3.1

DISCUSSION

In this investigation it was found that the flow stress, the strain rate sensitivity, the temperature dependence of flow stress and the activation volume were strongly dependent on the nitrogen content. Skaggs (48) reported that the flow stress of electrotransport purified thorium showed only an extremely small contribution from thermally activated processes. Based on these facts, it is reasonable to assume that the important thermally activated deformation processes in thorium are those involving solute atoms. Thermally activated processes which involve solute atoms include the interaction of dislocations with randomly dispersed solute atoms and with regions of solute segregation such as Cottrell atmospheres, precipitates and solute stabilized stacking faults. The thorium-nitrogen alloys in this study were most probably random interstitial solid solution. This conclusion was based on the linear increase in both the resistivity and lattice parameter with nitrogen content. Also, it was found that, at a given temperature, the flow stress and strain rate sensitivity were constant functions of the nitrogen concentration. If these alloys deviated significantly from randomness, the relationship between these physical parameters would change in going from a dilute solid solution to a more concentrated solid solution. Also aging was detected only in the alloys above the nitrogen solubility limit, 0.58 a/o and 0.97 a/o

nitrogen, and then only at temperature above 200°C.

Friedel (27) has proposed a model in which solute atoms act as short range barriers to dislocation motion. His model predicts that the flow stress-temperature relationship for a random solid solution would be approximated as follows:

$$\tau - \tau_{\mu} \approx (\tau_0 - \tau_{\mu}) \left(1 - \frac{T}{T_c}\right)^n \quad \text{for } T \ll T_c \quad (7)$$

$$\tau - \tau_{\mu} \approx 0 \quad \text{for } T \gg T_c \quad (8)$$

where n , τ_0 and T_c are constants which depend on the solute concentration. The critical temperature, T_c , is the temperature at which $\tau - \tau_{\mu} = 0$ and for thorium-nitrogen alloys was found to be approximately 360°K. τ_0 is the shear stress at absolute zero, T is the temperature and τ_{μ} is the athermal shear stress. For a concentrated solution, where the solute concentration is greater than about 10^{-2} a/o, $n = 1$ and a linear decrease in the flow stress with increasing temperature is predicted up to T_c . This prediction is followed, as shown in Figure 5, except for alloys containing 0.58 and 0.97 a/o nitrogen which deviated from the linear temperature dependence at low temperatures. This deviation will be discussed later in this section in connection with the concentration dependence of the flow stress.

The activation volume, according to Friedel's model, would be independent of stress and temperature up to T_c for a concentrated solution, $C > 10^{-2}$ a/o. It was found that from

77°K to 273°K the activation volumes were nearly constant with temperature up to the critical temperature. This change in the activation volume with temperature is due to the fact that the strain rate sensitivity has a maximum at 273°K which is below T_c . One explanation of this might be due to a range of interaction energies between the solute atoms and the dislocations, rather than a single energy barrier as used in Friedel's model. Nitrogen atoms situated such that they have a smaller interaction energy with the glissile dislocations would have lower critical temperatures. This would lead to an increase in the activation volume when the critical temperature of some of the nitrogen atoms had been exceeded. Such a range of interaction energies is not in agreement with the results obtained from the constant stress measurements. In these tests, it was found that the strain rate parameter and consequently the activation volume were constant over a large range of stress for a given alloy at a given temperature as shown in Figure 13. This behavior would indicate that the barriers have a fairly narrow range of interaction energies.

Another assumption that is made in Friedel's model is that the glissile dislocation density is constant. The validity of this assumption could be questioned if the range of deformation temperature is large. As the deformation temperature is changed, a different mobile dislocation density is possible for a given amount of strain. Variation in the mobile dislocation density, from one set of test conditions

to another, could affect the observed flow stress and activation volume. In a material in which a thermally activated deformation process is important, the effect could be significant.

Friedel's model predicts that the activation energy should be independent of concentration and increase linearly with temperature up to nearly T_c . The activation energy was found to be independent of concentration within the limit of the measurements. The activation energy increased linearly with temperature up to 273°K but at higher temperatures it increased more rapidly than linear. Again this deviation from the model is due to the maximum in the strain rate sensitivity occurring at a temperature below T_c .

One of the more interesting results of this investigation was the change from a first power dependence of the flow stress on concentration in the temperature range 198°K to 360°K to a dependence on the square root of concentration at 77°K and 4.2°K. Friedel's model predicts a linear dependence of flow stress with solute content for a concentrated solid solution, $C > 10^{-2}$ a/o, and a square root dependency for a very dilute solid solution, $C < 10^{-2}$ a/o. The results found here do not support this form of concentration dependence. An explanation of this behavior may be correlated to the distance between the obstacles along the dislocation length. As stated in the introduction, this spacing is one of the parameters which appears in equations for flow stress-concentration

dependency. The spacing of obstacles along the length of a mobile dislocation is a function of at least two variables, the mean distance between obstacles and the strength of those obstacles. For a given alloy, the concentration is constant with temperature and hence the mean distance between barriers remains unchanged. Since the obstacles in this system are of such a nature that thermal fluctuation aids the dislocation in surmounting them, the effective barrier strength increases as the test temperature decreases. This stronger interaction requires a higher stress to move the dislocation and the dislocation will bow to a smaller radius between the obstacles. This flexing allows the dislocation to come into contact with other obstacles and results in a smaller spacing along the dislocation such that $L \approx b/\sqrt{2c}$. This smaller spacing would result in a square root dependency of flow stress on concentration because $\tau \approx \mu b/L$.

Different types of atomic defects may cause vastly different amounts of hardening at a given concentration. Fleischer (49) has reviewed the data on solid solution hardening and separated it into two groups, depending on the observed hardening of various crystals by different types of defects. The first group is described as "gradual" hardening and is due to impurities which have high symmetry. An example of this type of hardening is the spherical distortion of the lattice by atomic size mismatch considered by Mott and Nabarro (19, 20). "Gradual" hardeners increase the shear stress per unit

concentration by $d\tau/dc < 1/10\mu$. The second group of defects considered were those that show "rapid" hardening in which the lattice distortions are highly asymmetrical and result in a $d\tau/dc > 2\mu$.

Fleischer (23) has pointed out that the interaction between a screw dislocation and an atomic defect producing a spherical distortion will be, in general, very small or zero. Therefore, strengthening caused by a spherical distortion of the lattice would not be as effective a strengthening agent as one producing a tetragonal distortion. In face centered cubic metals, a spherical distortion will be produced by an interstitial solute atom in either the tetragonal sites or the octahedral sites. Thus it would seem that the strengthening effect of an interstitial atom in face centered cubic metals should fall into the "gradual" hardening category. Figure 7 shows the variation of the shear stress of thorium at 4.2°K as a function of nitrogen content. Using $3.9 \times 10^{+6}$ psi for the shear modulus, the increase in the shear stress per unit concentration is then $d\tau/dc = 0.35\mu$. The strengthening rate of nitrogen in thorium falls between the "gradual" and the "rapid" hardeners.

The specific increase in the lattice parameter with nitrogen content, $1/a_0 da_0/dc$, was found to be small, 0.067. Hence, a small elastic interaction energy between an edge dislocation and a nitrogen atom is expected. Using an equation proposed by Bilby (50), the elastic interaction energy between

an edge dislocation and a nitrogen atom at a distance of one atomic diameter ($3.6 \text{ \AA}$) was calculated to be about 0.08 electron volts. This result is negligible compared to the observed activation energy for plastic deformation of 1.2 electron volts. The interaction between a nitrogen atom and dislocation is much stronger than that predicted from the spherical distortion produced by a nitrogen atom in an octahedral position.

Thorium nitride has a face centered cubic crystal structure with nitrogen atoms in octahedral holes surrounded by six thorium nearest neighbors. This same atomic arrangement seems likely for nitrogen in solid solution in thorium. The energy to form the six thorium-nitrogen bonds at 25°C was estimated by adding the following reactions:

Since a value for the enthalpy of formation of thorium nitride was not available, an approximate value was estimated by setting it equal to the enthalpy of formation for Th_3N_4 of -78 kcal/mole N (51). This value should be somewhat on the low side. The heat of solution of ThN in thorium was determined by Gerds and Mallett (36). The energy to form six thorium-

nitrogen bonds is 180 kilocalories per mole, 30 kilocalories per bond or 1.3 electron volts per thorium-nitrogen bond. Rundle (52) has proposed a covalent bonding mechanism for sodium chloride structure phases such as ThN. The interstitial atom was assumed to form six resonating covalent bonds with the six nearest metal neighbors. The lattice strain of a dislocation near a nitrogen atom in solution would change the length and orientation of these bonds and hence their energy. If the dislocation destroyed one of the nitrogen-thorium bonds, the interaction energy would be 1.3 electron volts which is very close to the observed activation energy for deformation. The activation energy for diffusion of nitrogen in thorium is 0.98 electron volts which is also quite close to the above values. The bond energy model (26) seems to be applicable and can be used to explain the large strengthening which nitrogen produces in thorium.

The formation of precipitate particles can greatly strengthen an alloy. To understand this increase in strength one must study in detail the ways in which dislocations interact with precipitate particles. A dislocation may cut through the particles or avoid them by moving to another slip plane or by bending between the particles leaving a dislocation ring around each precipitate. All of these processes require energy to be expended. The temperature of deformation, the nature of the precipitate and the applied stress are factors which can control which of these processes takes place. If

the particles have a high shear strength and are spaced far enough apart the dislocation may bow out between the particles in the glide plane as was suggested by Orowan (29). This process will leave a dislocation ring around the particles and increase the work hardening rate of the metal (53). The flow stress necessary to bow a dislocation between precipitate particles will depend on temperature through the temperature coefficient of the shear modulus only. A dislocation can also move to another slip plane by climb or cross slip to avoid the precipitate particles. Thermal activation may be involved in both climb or cross slip, hence a flow stress controlled by these processes decreases with increasing temperature. For a dislocation to shear a particle, energy must be supplied to drive the shear strain through the particle. The shearing process may be aided by thermal fluctuation if the dimensions of the particle are small.

In the previous section it was concluded that the temperature dependence of the flow stress of the aged alloys between 0°K and 333°K was due to the residual nitrogen in solution. Also, it was indicated that below 333°K the ThN particles present an athermal barrier to dislocation movement. The applied shear stress τ_a in this temperature region can be represented by

$$\tau_a = \tau^* + \tau_\mu^m + \tau_\mu^p \quad (9)$$

where τ^* is the thermal component of the shear stress, τ_μ^m is

the athermal component of the matrix and τ_{μ}^P is the athermal component due to the precipitate particles. It has been shown by Ebeling and Ashby (54) that the contributions to the shear strength of a crystal are additive as indicated by Equation 9. The athermal component of the flow stress at 0°K increased from 8900 psi for the quenched solid solution alloys to 21,000 psi and 34,000 psi for the aged alloys which contained 0.58 a/o and 0.97 a/o nitrogen, respectively. The precipitate particles, which are athermal obstacles below 523°K, become subject to thermal activation above this temperature. From 523°K to 623°K, the thermal fluctuations are large enough to assist dislocations in overcoming the barriers presented by the thorium nitride particles. This new thermal component gave rise to an increase in the strain rate sensitivity and the temperature dependence of flow stress in this temperature range.

The activation volume and energy were determined from $\Delta\sigma^*/\Delta T$, and $\Delta\sigma/\Delta \ln \dot{\epsilon}$, obtained from Figures 21 and 22. The calculated values of the activation energies and volumes in the temperature range of 0°K to 333°K were the same as that obtained for the solid solution hardened alloys containing between 0.32 a/o and 0.58 a/o nitrogen. The activation volumes observed for the aged alloys from 523°K to 623°K were $125 b^3$ for the 0.58 a/o nitrogen alloy and $65 b^3$ for the 0.97 a/o nitrogen alloy. The activation volumes obtained for age-hardened aluminum alloys reported by Kelly (53) ranged from

$250 b^3$ to $740 b^3$. These activation volumes indicate that the thorium nitride particles must be very small and probably are smaller than the precipitates responsible for age-hardening in some aluminum alloys. The activation energies associated with the thorium nitride precipitate was 3.0 electron volts. The energies reported for aged aluminum alloys ranged from 3.7 to 9.0 electron volts.

The true stress-true strain curves show that the work hardening rates for the aged alloys are the same as that for the unaged alloys. This behavior would indicate that Orowan's mechanism is not active, as this mechanism is associated with a very high rate of work hardening (53). Cross slip does not seem likely as edge dislocations can not cross slip, and hence would be blocked by precipitate particles. Ashby (55) used a modification of Orowan's theory, following Hirsch (56), to explain how an edge dislocation could bypass particles by double cross slip. This process leaves both a prismatic dislocation loop around the particle and a corresponding prismatic jog in the dislocation line. This type of mechanism would most likely increase the work hardening rate in a manner similar to that produced by the Orowan's mechanism. At these temperatures and strain rates, climb can be eliminated as a possible means of avoiding the particles, as climb is a diffusion controlled process. For climb to be considered as possible mechanism the temperature of the material must be sufficiently high so that diffusion is rapid. Therefore, the

precipitate particles are most probably sheared by dislocations during deformation as is found to be the case in many precipitation hardened alloys. In order to define the exact deformation mechanism and to make a comparison between the experimental results and theoretical predictions, a study on a wider range of particle radii and concentrations would be required.

CONCLUSIONS

Nitrogen strengthens thorium primarily by presenting short range barriers to dislocation movement. At temperatures below 360°K these short range barriers give rise to a thermally activated component of the flow stress which increases with decreasing temperature. The thermally activated component increases linearly with nitrogen content at temperatures above 198°K and increases with the square root of the nitrogen content at 77°K and 4.2°K. It is this thermally activated component of flow stress which leads to a strain rate dependence of the flow stress. The strain rate sensitivity goes through a maximum at 273°K and was found to increase with nitrogen content. The interaction between glissile dislocations and nitrogen atoms appears to have a strength of about 1.2 eV. In the solid solution alloys tested, the athermal component was found to be nearly independent of temperature and nitrogen content.

Age hardenable alloys could be produced from the thorium-nitrogen alloys containing 0.58 a/o and 0.97 a/o nitrogen. This was accomplished by quenching from 1000°C to produce a supersaturated solid solution which was then aged at 300°C for 16 hours. This aging produced thorium nitride particles of less than 10 atom diameters, $36\text{\AA}$, in size which greatly increased the flow stress of the metal. In the temperature range from 0°K to 333°K the thorium nitride particles strength-

ened the alloy by increasing the athermal component of the flow stress with the residual nitrogen left in solution resulting in a thermally activated component of flow stress. At higher temperatures, 523°K to 623°K, the thorium nitride particles gave rise to an athermal component of flow stress which decreases with increasing temperatures.

BIBLIOGRAPHY

1. R. Becker, Physikalische Zeitschrift, 26, 919 (1925).
2. A. Seeger in "Proc. 2nd International Conf. on the Peaceful Uses of Atomic Energy," United Nations Publication, New York, 1958, Vol. 6, p. 250.
3. H. Conrad and H. Wiedersich, Acta Metallurgica, 8, 128 (1960).
4. H. Conrad, Journal of the Iron and Steel Institute, 198, 364 (1961).
5. Z. S. Basinski, Philosophical Magazine, 4, 393 (1959).
6. D. P. Gregory, Acta Metallurgica, 11, 455 (1963).
7. I. C. M. Li in "Dislocation Dynamics," A. R. Rosenfield, G. T. Hahn, A. L. Bement, Jr., and R. I. Jaffee, Eds., McGraw-Hill, New York, 1968, p. 87.
8. A. H. Cottrell in "Report of a Conference on Strength of Solid," University of Bristol, Physical Society of London, 1948, p. 30.
9. A. H. Cottrell, "Dislocations and Plastic Flow in Crystal," Oxford University Press, London, 1953, p. 125.
10. H. Suzuki in "Dislocation and Mechanical Properties of Crystals," J. D. Fisher, W. G. Johnston, R. Thompson, and T. Vreeland, Jr., Eds., John Wiley, New York, 1956, p. 361.
11. J. Fisher, Acta Metallurgica, 2, 9 (1954).
12. R. Peierls, Physical Society of London, Proceedings, 52, 34 (1940).
13. F. R. N. Nabarro, Physical Society of London, Proceedings, 59, 256 (1947).
14. H. Conrad in "The Relation between the Structure and Mechanical Properties of Metals," National Physical Laboratory Symposium No. 15, Her Majesty's Stationery Office, London, 1963, p. 476.
15. J. Snoek, Physica, 6, 591 (1939).

16. A. H. Cottrell, S. C. Hunter, and F. R. N. Nabarro, Philosophical Magazine, 44, 1064 (1953).
17. N. P. Allen, T. H. Schofield, and A. E. L. Tate, Nature, 168, 378 (1951).
18. N. G. Ainslie, R. W. Guard and W. R. Hibbard, Transactions of the Metallurgical Society of AIME, 215, 42 (1959).
19. N. F. Mott and F. R. N. Nabarro in "Report of a Conference on Strength of Solid," University of Bristol, Physical Society of London, 1948, p. 1.
20. N. F. Mott in "Imperfection in Nearly Perfect Crystals," W. Shockley, Ed., John Wiley and Sons, New York, 1952, Chapter 6.
21. D. McLean, "Mechanical Properties of Metals," John Wiley and Sons, New York, 1962, p. 178.
22. J. Friedel, "Les Dislocations," Gauthier-Villars, Paris, 1956, English edition (enlarged) Pergamon Press, Oxford, 1964, p. 363.
23. R. L. Fleischer, Acta Metallurgica, 9, 996 (1961).
24. R. L. Fleischer, Acta Metallurgica, 11, 203 (1963).
25. R. L. Fleischer and W. R. Hibbard in "The Relation between the Structure and Mechanical Properties of Metals," National Physical Laboratory Symposium No. 15, Her Majesty's Stationery Office, London, 1963, p. 261.
26. D. T. Peterson and R. L. Skaggs, Transactions of the Metallurgical Society of AIME, 242, 922 (1968).
27. J. Friedel in "The Relation between the Structure and Mechanical Properties of Metals," National Physical Laboratory Symposium No. 15, Her Majesty's Stationery Office, London, 1963, p. 409.
28. N. F. Mott and F. R. N. Nabarro, Physical Society of London, Proceedings, 52, 86 (1940).
29. E. Orowan, [Discussion] in "Symposium on Internal Stress in Metal and Alloys," Institute of Metals, London, 1948, p. 451.

30. F. R. N. Nabarro in "Symposium on Internal Stress in Metal and Alloys," Institute of Metals, London, 1948, p. 237.
31. R. W. K. Honeycombe, "The Plastic Deformation of Metals," St. Martin's Press, New York, 1968, p. 178.
32. A. Kelly, A. Lassila, and S. Sato, Philosophical Magazine, 4, 1260 (1959).
33. A. Kelly and M. E. Fine, Acta Metallurgica, 5, 365 (1957).
34. Byrne, J. G., M. E. Fine, and A. Kelly, Philosophical Magazine, 6, 1119 (1961).
35. R. Mickelson and D. Peterson, Transactions American Society for Metals, 50, 340 (1958).
36. A. F. Gerds and M. W. Mallett, Journal of the Electrochemical Society, 101, 175 (1954).
37. D. T. Peterson, W. E. Krupp and F. A. Schmidt, Journal of the Less Common Metals, 7, 288 (1964).
38. D. T. Peterson and D. G. Westlake, Journal of Physical Chemistry, 64, 649 (1960).
39. T. A. Despres in "Symposium on Electron Metallography," American Society for Testing and Materials, Philadelphia, Pa., 1963, p. 24.
40. D. T. Peterson, D. F. Page, R. B. Rump and D. K. Finne-
more, The Physical Review, 3, 701 (1967).
41. R. P. Zerwekh and T. E. Scott, Trans. of the Metallurgical Society of AIME, 239, 432 (1967).
42. D. C. Zabel, II, "The Effect of Zirconium on the Strength of Thorium," M.S. thesis, Iowa State University, Ames, Iowa, 1972.
43. P. E. Armstrong, O. N. Carlson and J. F. Smith, Journal of Applied Physics, 30, 36 (1959).
44. G. Y. Chin, W. F. Hosford, Jr. and W. A. Backofen, Trans. of the Metallurgical Society of AIME, 230, 437 (1964).
45. I. G. Kaufman, K. O. Bogardus and E. F. Wanderer in "Advances in Cryogenic Engineering," K. D. Timmerhaus, Ed., Plenum Press, New York, 1968, Vol. 13, p. 294.

46. C. J. Guntner and R. P. Reed in "Advances in Cryogenic Engineering," K. D. Timmerhaus, Ed., Plenum Press, New York, 1961, Vol. 6, p. 565.
47. Z. S. Basinski, Proceedings of the Royal Society of London, A240, p. 229 (1957).
48. R. L. Skaggs, "The Effect of Carbon on the Strength of Thorium," Ph.D. thesis, Iowa State University, Ames, Iowa, 1967.
49. R. L. Fleischer, Acta Metallurgica, 10, 835 (1962).
50. R. A. Bilby, Physical Society of London, Proceedings, A63, 191 (1959).
51. L. S. Darken and R. W. Gurry, "Physical Chemistry of Metals," McGraw-Hill Book Company, Inc., 1953, p. 370.
52. R. E. Rundle, Acta Crystallographica, 1, 180 (1948).
53. A. Kelly in "Electron Microscopy and Strength of Crystal," G. Thomas and J. Washburn, Eds., Interscience Publishers, New York, 1963, Chapter 22.
54. R. Ebeling and M. F. Ashby, Philosophical Magazine, 13, 805 (1966).
55. M. F. Ashby in "Electron Microscopy and Strength of Crystals," G. Thomas and J. Washburn, Eds., Interscience Publishers, New York, 1963, Chapter 19.
56. P. B. Hirsch, Appendix to paper by G. Thomas and J. Nutting, Journal of the Institute of Metals, 86, 7 (1957).

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