

THE SURFACE AND GRAIN BOUNDARY FREE ENERGIES
OF PURE TITANIUM AND THE TITANIUM ALLOY Ti-6Al-4V

by

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ABSTRACT

The zero-creep of fine wires technique has been used to obtain the absolute values of surface and grain boundary free energies over a range of elevated temperatures in a purified helium atmosphere and under equilibrium conditions for pure titanium metal and the Ti-6Al-4V alloy, a principal metal and alloy used in the aerospace industry. The corresponding elevated temperature coefficients of the interfacial free energies and the ratio of grain boundary to surface free energy have also been determined. The creep of fine wires of the two materials whose grain boundaries form a "bamboo" structure under creep conditions is assumed to be linearly controlled by the Nabarro-Herring mechanism. The values of the self-diffusion coefficients of pure titanium and the Ti-6Al-4V alloy have been obtained and compared by using this model. The interfacial free energy and self-diffusion coefficient values for pure titanium are found to be smaller than those of the Ti-6Al-4V alloy. Comparison of the results of this study with values reported in the literature gives good agreement. It is believed that the results obtained in this work are the true values for the materials under the conditions of the investigation.

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CHAPTER I

INTRODUCTION

The pressing need in the aircraft industry for a high strength, light weight material useful at elevated temperature has led to a considerable amount of development work on pure titanium and titanium alloys. By utilizing titanium-base alloys, it will be possible to design and produce aircraft to operate at speeds which involve skin temperature in excess of those that can be tolerated by conventional material such as aluminum. Its lower density (which lies roughly half-way between aluminum and iron) permits production of planes of greater maneuverability, longer range and striking power at higher speeds. The major advantage of this metal results from the high strength to weight ratio at temperatures ranging from -423°F to $+1100^{\circ}\text{F}$. At room temperature, pure titanium shows little superiority over some of the stronger aluminum or magnesium alloys. However, at slightly elevated temperature, the light alloys lose strength rapidly while titanium retains much of its strength up to at least 800°F . Titanium and its alloys also have excellent toughness, fatigue strength and corrosion resistance. Thus, titanium is a metal of great commercial and military aircraft potentiabilities.

Titanium has a close-packed hexagonal crystal structure, called alpha, which transforms to a body-centered cubic structure, called beta, at 1620°F (882°C). Basically, pure titanium is soft, weak and extremely ductile. However, through appropriate additions of alloying elements the titanium metal is converted to a material with higher strength and excellent in fracture toughness, ductility and corrosion resistance. The alloying elements added to titanium tend to stabilize either the alpha or the beta phase. Elements that preferentially dissolve in the

alpha phase are termed alpha stabilizers and elements which are more soluble in the beta phase are termed beta stabilizers.

Ti-6Al-4V, a titanium alloy with approximately 6% aluminum and 4% vanadium, is the most widely used of all the titanium alloys. This type of alloy has a mixed alpha-beta microstructure and is distinguished by its high tensile strength at elevated temperature, good thermal stability and high hydrogen-tolerance. Due to these superior characteristics, the alloy is widely used in airframes, turbine engine parts, ordnance equipment, pressure vessel and rocket motor cases.

An important problem in the application of titanium metal and its alloy to high temperature service in the aircraft is the severe degradation of yield strength, fracture toughness and thermal fatigue resistance under conditions of long hold periods. The mechanical properties of these engineering materials can be explained, controlled and improved from the study of surface and grain boundary phenomena.

The surface and grain boundary free energies of the solid metals are of special interest because of their powerful influence on technically important processes such as high temperature stress induced cavity formation, fracture toughness, sintering and creep.

It is necessary, therefore, that the reliable values of surface and grain boundary free energies of pure titanium and Ti-6Al-4V alloy should be obtained for the use of estimating the ideal strength and thereby providing useful aircraft and missile materials design criteria at elevated temperature.

The surface and grain boundary free energies of solid metals are difficult to measure at best. There have been numerous attempts to calculate the surface and grain boundary free energies of metals and alloys

on both an empirical (Breger and Zhukhoritskii,1946; Stratton,1953; Zadumkin,1955; Skapski,1956; Zadumkin,1961; Semenchenko,1962; Zadumkin,1963; Avraamov and Gvozdev,1967; Zadumkin et al.,1968; Missol,1973) and a theoretical basis (Frenkel,1928; Bardeen,1936; Hohenberg and Kohn,1964; Kohn and Sham,1965; Smith,1969; Lang and Kohn,1970; Rouhani and Schattler, 1973) but the discrepancies between calculated and experimentally determined surface free energies have been so great in many instances as to make the calculational schemes nearly impractical as a general formulation for all metals. Theories of metal surface have been lacking primarily because of the difficulties in dealing with the decrease of electron density near the surface and the loss of translational symmetry at the surface. So far, the "zero-creep technique" (Udin et al.,1949) has provided the majority of reliable experimental values of surface and grain boundary free energies of solid metals and alloys at elevated temperatures. This technique relies on the basis that at elevated temperatures where flow of solid metals can take place under low stresses, the surface free energy can be determined by placing small weights at the end of a wire or foil and determining the weight just necessary to balance the surface free energy. By using this technique for small diameter wires whose grain boundaries have ideally formed a "bamboo" structure and measurements of the dihedral angle at the base of thermally etched grain boundary grooves, absolute values of the surface and grain boundary free energies can be found.

OBJECTIVES

The purpose of this study is an investigation of the absolute surface and grain boundary free energies, at elevated temperatures and under equilibrium conditions, of pure titanium metal and Ti-6Al-4V alloy

which are a principal metal and alloy having present day use as aircraft and spacecraft structural materials. The study is designed to obtain the basic experimental information by using the zero-creep of fine wires technique for the undetermined surface free energy, grain boundary free energy, and the corresponding elevated temperature coefficients of pure titanium and the Ti-6Al-4V alloy. Under creep conditions, the deformation of fine wires is assumed to be linearly controlled by the Nabarro-Herring mechanism. Using this model, the self diffusion coefficients of both pure titanium and the Ti-6Al-4V alloy at elevated temperatures will also be determined and compared.

CHAPTER II

LITERATURE REVIEW

TITANIUM AND ITS ALLOYS

General

Titanium is a light, non-magnetic metal, weighing 45% less than steel and only 60% more than aluminum. It is the fourth most abundant structural metal in the earth's crust and ninth most common element. Titanium has a lower linear coefficient of expansion and lower thermal conductivity than either aluminum or alloy steels. Its tensile modulus of elasticity lies midway between steel and aluminum. Comparison in physical properties of pure titanium and other pure metals are shown in Table 1.

Physical Metallurgy of Titanium

Titanium, being allotropic, can exist in two crystal forms known as alpha (which has the hexagonal close-packed crystal structure) and beta (which has the body centered cubic structure). In pure titanium, the alpha phase is stable at all temperatures up to approximately 1620°F (882°C) where it transforms to the beta phase. The temperature of transformation is known as the beta transus temperature. The beta phase is stable from 1620°F to the melting point of about 3140°F (1730°C).

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Table 1. Physical Properties of Pure Titanium Compared to Other Pure Metals
(From 'Basic Design Facts About Titanium', Reactive Metals Inc.,
Niles, Ohio, Bulletin no. 1000-6606).

Properties	Titanium	Magnesium	Aluminum	Iron	Copper
Atomic Number	22	12	13	26	29
Atomic Weight	47.90	24.32	26.97	55.85	63.57
Density (lbs/cu.in.)	0.163	0.063	0.098	0.284	0.324
Melting point (°C)	1730	650	660	1539	1083
Melting point (°F)	3140	1202	1220	2802	1981
Coefficient of Linear Expansion (10^{-6} in/in/°F) (32-212°F)	5.0	14.4	13.2	6.5	9.4
Thermal Conductivity (Btu/hr/ft ² /°F/ft)	9.0	56	117	46	221
Specific Heat (Btu/lb/°F) at R.T.	0.126	0.246	0.215	0.107	0.092
Electrical Resistivity (microhm-cm at R.T.)	47.8	4.6	2.824	10.0	1.724
Tensile Modulus of Elasticity ($\times 10^6$ lb/sq.in.)	16.5	6.5	10.0	28.5	17

Titanium grades fall into three major classes, depending on the phase, or phases, present in their microstructures: alpha, mixtures of alpha and beta, and beta. The grades that consist largely of the alpha phase are classified as alpha alloys. The grades that contain mixtures of alpha and beta phases are classified as alpha-beta alloys, and the grades that consist largely of the beta phase on cooling from the solution annealing temperature are termed beta alloys. It should be pointed out, however, that most grades of unalloyed titanium and certain alpha alloys contain small amounts of beta stabilizing elements, while the beta alloys contain small amounts of alpha stabilizing elements as strengthening agents. Each system of titanium alloys has certain distinguishing characteristics.

Alpha alloys. The hexagonal structured compositions possess the highest strength and oxidation resistance at elevated temperatures (600-1000°F) and the best weldability of the titanium grades. Room temperature strength levels, however, are lowest and these compositions do not respond to heat treatment.

Within the alpha alloy classification are commercially pure (or unalloyed) titanium and alloys with high aluminum contents. In commercially pure titanium, as in all other metals, as strength goes up, toughness, ductility and formability go down. Thus, the softest titanium grade provides the highest formability.

Alpha-Beta alloys. As a class, alpha-beta alloys have higher strength and respond to heat treatment but are less formable than alpha alloys. This class of titanium alloys accounts for more than half of all titanium used.

The alpha-beta alloys vary widely in composition and therefore, in their general characteristics. At one end of the alloy range are the highly

beta stabilized alloys such as Ti-7Al-4Mo and Ti-6Al-6V-2Sn, which provide high strength at room and intermediate temperatures. At the other end are the lean alpha-beta compositions, such as Ti-6Al-4V. Ti-6Al-4V is considered as the "general purpose" titanium alloy because of its comparatively high aluminum content that gives it such excellent strength and elevated temperature properties.

Beta alloys. Titanium can also be made to exist entirely in the beta phase at room temperature. This is accomplished with alloy additions which inhibit the beta-to-alpha transformation. The beta or near-beta alloys are highly heat treatable. They are capable of high strengths, have fair creep resistance and good formability.

Titanium-base alloys are similar to many other engineering metals. Pure titanium metal is soft, weak and extremely ductile. However, through appropriate additions of other elements the titanium metal base is converted to an engineering material with unique characteristics, high strength and stiffness, useable ductility, corrosion resistance and lower density than most other structural metals. The most predominate of these characteristics in any given composition is a function of the alloying additions selected.

Effects of Alloying Elements

The selective addition of alloying elements to titanium enables a wide range of physical and mechanical properties to be obtained. As alloying elements are added to it, they tend to change the temperatures at which the phase transformation occur and the amount of each phase present. Alloy additions to titanium tend to stabilize either the alpha or the beta phase. Elements that preferentially dissolve in the alpha phase stabilize this phase to higher temperatures are termed alpha stabilizers. The elements

which are more soluble in the beta phase tend to stabilize this phase to lower temperatures and are termed beta stabilizers.

In attempting to describe microstructural changes based on constitution or equilibrium diagrams, it is convenient to use the binary systems. However, it should be kept in mind that the binary diagrams offer only an approximation of the actual conditions being considered since most commercial alloys of titanium are of the ternary or quaternary type. Furthermore, production processes seldom approach equilibrium conditions.

Alpha Stabilized System

Fig. 1 represents an approximation of the binary constitution diagram for an alpha stabilized system. In this system the addition element is more soluble in the alpha phase and an increase in the alloy content stabilizes the alpha phase to higher temperatures. That is, both the alpha and beta transformation temperatures are raised by increasing the alloy content. Some of the alloying elements of the substitutional type that belong to this system are aluminum, gallium and germanium. The interstitial alloying elements of the alpha stabilizing type are oxygen, nitrogen and carbon.

Beta Stabilized System

The beta stabilized system can be broken down into two types; the beta isomorphous and the beta eutectoid. Fig. 2 shows an approximate binary constitution diagram for the beta isomorphous system. In this system the addition element is completely miscible in the beta phase and decomposition of beta to alpha plus eutectoid products does not occur even under equilibrium conditions. Increasing the alloy content decreases the alpha-to-beta transformation temperature. Alloy elements of the beta isomorphous type are vanadium, molybdenum, tantalum and columbium.

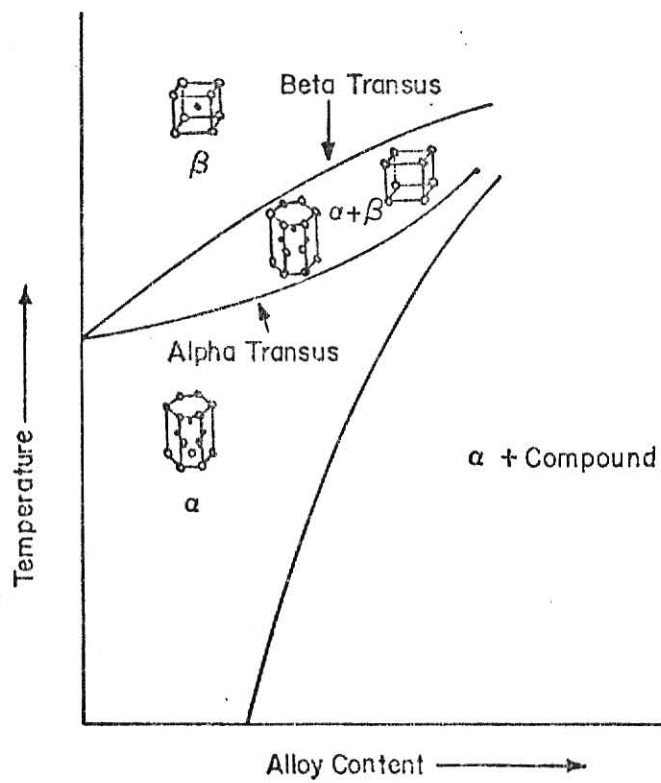


Fig. 1. ALPHA STABILIZED SYSTEM: Alpha Stabilizing Elements are Aluminum, Gallium, Germanium, Carbon, Oxygen and Nitrogen.

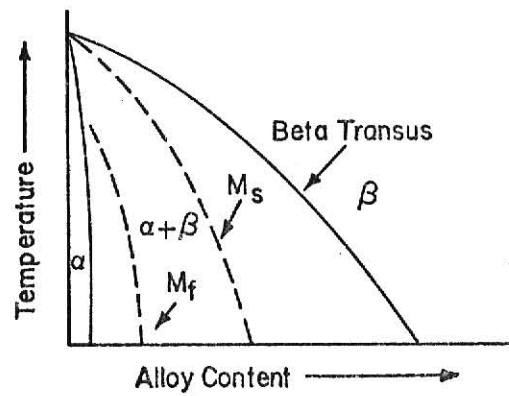


Fig. 2. BETA ISOMORPHOUS SYSTEM: Alloying Elements of the Beta Isomorphous Type are Vanadium, Molybdenum, Tantalum and Columbium.

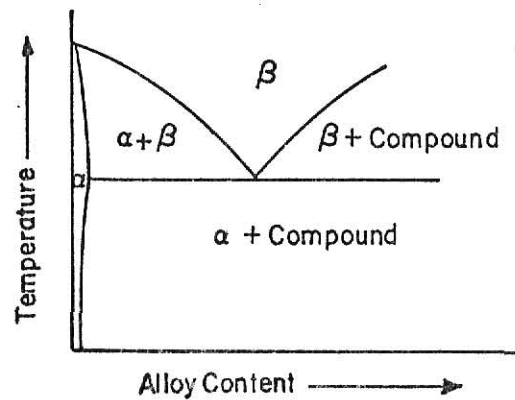


Fig. 3. BETA EUTECTOID SYSTEM: Alloying Elements of the Beta Eutectoid Type are Manganese, Iron, Chromium, Cobalt, Nickel, Copper and Silicon.

Fig. 3 represents the approximate binary phase diagram of the beta eutectoid system. In this system the addition element stabilizes the beta phase, but under equilibrium conditions the beta phase decomposes to form alpha and an intermetallic compound. The beta eutectoid elements are of two types, the active eutectoid and the sluggish eutectoid formers. Active eutectoid formers, such as copper and silicon, result in rapid decomposition of beta to compound. Elements of this type have not been used extensively in commercial alloys. The other eutectoid formers, such as chromium, cobalt, nickel, iron and manganese are more sluggish in their eutectoid reactions and are not generally used in sufficient quantity to form compounds in most commercial alloys.

Tin and zirconium are interesting alloying elements in that they have extensive solid solubility in both the alpha and beta phases. These elements do not strongly promote phase stability, but do slow the reaction kinetics and are useful strengthening agents. As a consequence, they are attractive additions for both alpha and beta alloys.

Pure Titanium

Pure titanium is used where high ductility associated with moderate strength, high corrosion resistance and good weldability are desired. It is available in various degrees of purity, characterized mainly by different oxygen contents, and, consequently, with different mechanical properties. At room temperature, the tensile strength is about 52,000 psi., yield strength 36,000 psi., elongation 20% minimum, in 2 in.. The metal has considerable resistance to corrosion by many media of severely corrosive type, and this corrosion-resistance is found in many instances at temperatures up to 100°C (212°F) and above.

Impurity Effects in Pure Titanium

Pure titanium contains varying amounts of impurities such as oxygen, nitrogen, hydrogen and carbon. When they are present in significant amounts, these elements have a marked effect on the mechanical properties of titanium. However, these elements have almost no effect on the physical properties or other important properties of the metal.

Presumably, the principal impurities in pure titanium are oxygen, nitrogen, hydrogen, carbon and iron. Titanium readily absorbs carbon, nitrogen and oxygen and all three greatly affect the tensile strength of titanium as shown in Fig. 4. Of these three elements, nitrogen has the greatest strengthening and hardening effect, and carbon the least. An addition of 0.15% nitrogen almost doubles the tensile strength, and increases the Vickers hardness by 100 points. Ductility decreases with increase in all three elements. So, with an increase of both oxygen and nitrogen content, the hardness increases rapidly and the ductility as measured by elongation and reduction of area falls off sharply. Therefore, the low contents of oxygen, nitrogen and carbon are necessary if ductile titanium is to be obtained.

At temperatures above 600°F, large quantities of hydrogen can be absorbed by pure titanium resulting in embrittlement of the metal. Unlike oxygen and nitrogen, however, absorbed hydrogen can be removed by heating the metal in a vacuum at elevated temperature.

Iron is another common impurity in titanium but its effect is much less drastic than those of the elements mentioned above.

Ti-6Al-4V Alloy

The Ti-6Al-4V alloy is the most widely used of all alpha-beta titanium alloy types. Due to such widespread availability over a long period of time,

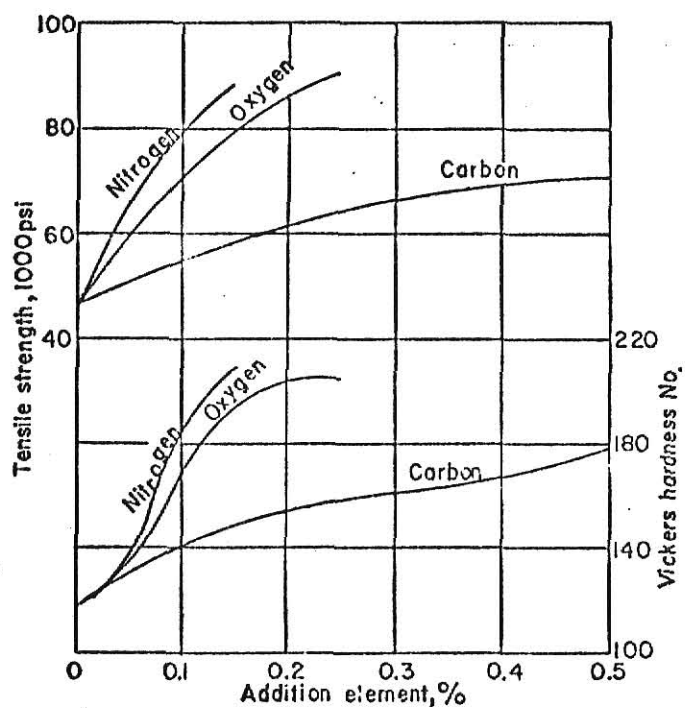


Fig. 4. Effect of Oxygen, Nitrogen and Carbon on the Strength and Hardness of Titanium (Finlay and Snyder, Trans. AIME, 188, 277, 1950.)

voluminous data and information for Ti-6Al-4V have been generated. Several grades of Ti-6Al-4V alloy are produced which differ from one another primarily in interstitial content, and also in aluminum, vanadium and iron content. A high-purity grade which has extra low interstitial (ELI) content is available for such uses as cryogenic tankage. Low interstitial grades also are being utilized for their higher fracture toughness. High interstitial content Ti-6Al-4V alloy is usually utilized in applications where the highest strength available, usually in the heat-treated condition, is desired. The standard grade contains an intermediate amount of interstitial elements and is the grade frequently used for airframes. The mechanical properties of this alloy are about 100,000-130,000 psi. tensile, 100,000-130,000 psi. yield strength and 5-10% elongation.

The composition for standard grade of Ti-6Al-4V alloys is illustrated in Table 2.

Physical Metallurgy of Ti-6Al-4V Alloy

The Ti-6Al-4V alloy is a classical example of a composition which utilizes both an alpha stabilizer (Al) and a beta stabilizer (V) to result in a two-phase (alpha plus beta) material. The 6 percent aluminum addition stabilizes the alpha phase of titanium to higher temperatures and strengthens this phase by a solid solution strengthening mechanism. The 4 percent vanadium addition is more than the amount soluble in the alpha phase, as shown in Fig. 5. Further, vanadium lowers the alpha-beta to beta transus temperature to about 1820°F, depending upon the exact composition of the alloy produced (Rausch, Crossley, and Kessler, 1956).

Effect of Aluminum and Vanadium in Titanium-Alloy

Titanium alloys in aircraft applications are primarily intended to serve at elevated temperature of 400 to 1000°F. At these temperatures,

Table 2. Composition for Standard Grade of Ti-6Al-4V Alloy
(From Aerospace Structural Handbook, Vol. 3, 1965).

Elements	Percent	
	Min.	Max.
Aluminum	5.50	6.75
Carbon	-	0.10
Hydrogen (bar)	-	0.0125
Hydrogen (sheet)	-	0.015
Iron	-	0.30
Nitrogen	-	0.05
Oxygen	-	0.20
Vanadium	3.50	4.50
Other elements total	-	0.40*
Titanium	Balance	

* Need not be reported

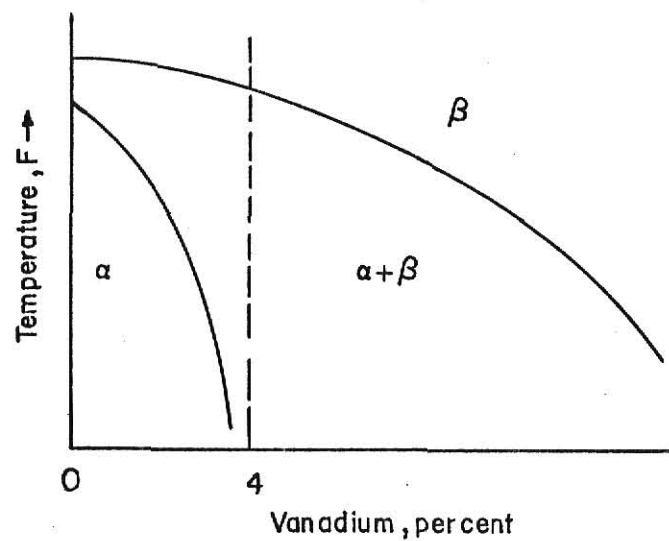


Fig. 5. Schematic Diagram Showing the Phase Relationships for the Ti-6Al-4V Alloy. (From Douglass, R.W., and Holden, F.C., TML Memorandum 148, 1958.)

creep and stability characteristics are the more important design parameters.

At the present time, the best combination of all properties of titanium alloy is shown by alpha-beta phase alloys. Alloys belonging to this class have good formability at high temperature. They can be mechanically worked and strengthened by heat treatment.

It is a general observation that aluminum which is a strongly alpha-phase stabilizer (with as little as 5% Al added, alpha-transus temperature is increased from 1620°F to 1778 °F and the corresponding beta-transus to 1823 °F) must be alloyed with titanium to achieve the best creep strength. Binary titanium-aluminum alloys, though single phase, non-heat treatable, and low in strength at room temperature, are yet of higher creep strength at elevated temperature than most high-strength, heat treated alloys containing only beta stabilizers. The usual range of titanium-aluminum alloys has been established as between 0 and 7.5% Al based on fabrication characteristics. In this α -alloy range, there is a moderate improvement in the oxidation resistance of titanium conferred by Al. The oxidation rate of titanium is lowered by about 40% by 8% Al. The improvement in oxidation rate by Al dose not result until over 4% Al is present. Contamination, as measured by hardness penetration into the metal, is not significantly affected by Al.

One of the prime advantages of using Al as an alloying addition to titanium is that it decreases the density of an already light metal. Unfortunately, only a relatively small amount of Al can be added while maintaining a ductile alloy. Of particular interest is the effect of Al on the density of alloys in the usable alloy range as shown in Fig. 6.

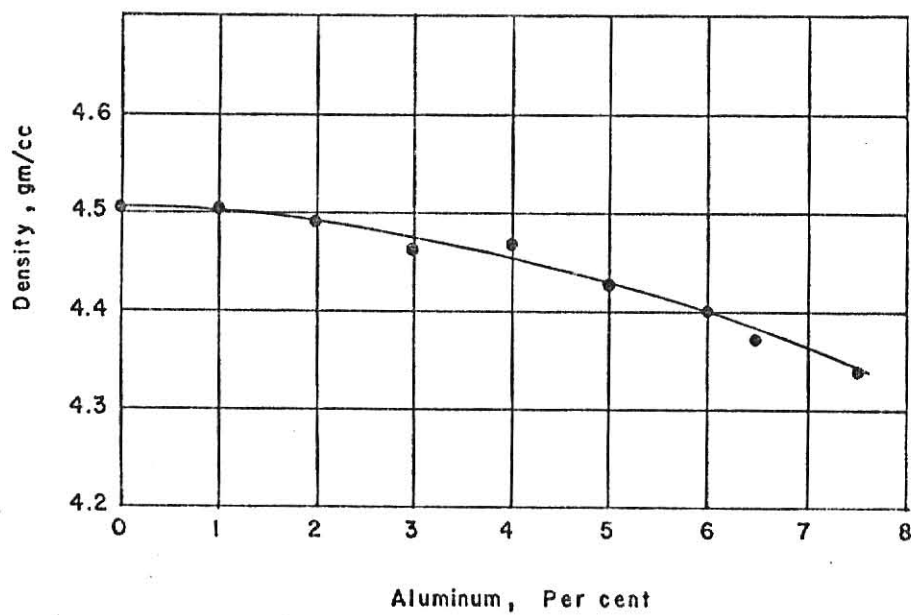


Fig. 6. Effect of Aluminum Content on the Density of High Purity Titanium. (Replotted from Ogden, H. R., et al., Trans. AIME, J. of Metals, 197, 271, 1953.)

The density is decreased significantly with increasing Al-content at the rate of about 0.02 g/cc. for each 1% Al added.

Titanium-aluminum alloys that contain small amounts of beta-phase stabilizers will precipitate a beta phase at room temperature. The alloys treated in this way acquire better properties (high plasticity and good weldability) and can be more easily mechanically worked than other alpha alloys. Vanadium which is a beta isomorphous stabilizer is widely used because of its relatively low specific gravity. This metal, however, is very expensive and difficult to obtain. Therefore, titanium alloys with a stable beta phase are not utilized to any great extent in industry.

Ti-6Al-4V alloy is currently regarded with considerable favor for a number of reasons. In its heat treated state, the creep strength of this alloy in the temperature ranging from 600°F to 900°F is superior to all but possible one (4%Al-4% Mn) commercial alloy. The alloy can be produced in both sheet and bar form. Its propensity to hydrogen embrittlement is considerably less than all beta stabilized alloys. After exposure to service stresses at elevated temperatures, it does not significantly gain or lose strength or ductility. Lack of stability at elevated temperatures is a common deficiency in titanium alloys.

Impurity Effects in Ti-6Al-4V Alloy

The general effects of small quantities of dissolved carbon, oxygen, and nitrogen on the Ti-6Al-4V alloy can be summarized as follows:

(1) The beta transus temperature for the standard grade of Ti-6Al-4V (containing up to a maximum of 0.10% carbon, 0.20% oxygen, and 0.05% nitrogen) is nominally $1825^{\circ}\text{F} \pm 25^{\circ}\text{F}$. Increasing amounts of these interstitial impurities increase this transus temperature.

(2) An increase in strength occurs with increased interstitial content. At low temperatures, $< -320^{\circ}\text{F}$, particularly when severe stress systems are involved, brittleness in high-interstitial-content alloys may occur. At intermediate temperatures, up to 500°F , an improvement in strength without an adverse loss of ductility is found. The strengthening effect of the interstitial decreases with increasing temperature.

(3) The transformation kinetics of the beta-to-alpha reaction are accelerated by the presence of these interstitials dissolved in the beta phase. However, for materials containing normal interstitial levels solution annealed in the alpha-beta field, most of the interstitial content is preferentially dissolved in the alpha phase, so that little or no effect on the transformation kinetics is observed.

(4) Notch sensitivity is increased by increased interstitial content, with the effects becoming more pronounced at low testing temperature.

The adverse effects of hydrogen in titanium alloys have been the subject of numerous investigations. It appears that, in comparison with other alpha-beta alloys, the Ti-6Al-4V alloy is relatively insensitive to hydrogen embrittlement so long as the hydrogen content is kept within specifications.

SURFACE AND GRAIN BOUNDARY FREE ENERGY OF SOLID METALS AND ALLOYS

General

The significance of surface and interfacial free energies are evident in determining the microstructure of polyphase systems in solid-state sintering, thermal etching of grain boundaries, heats of solution of fine powders, grain growth phenomena, mechanical behavior of fine fibers and foils, nucleation, the equilibrium configuration, wetting and flow properties in a solid-liquid-vapor systems, and other phenomena of academic or practical importance.

The source of an excess free energy in the surface of a phase may be visualized by considering the surroundings of an atom on the surface and in the interior as illustrated in Fig.7. At the surface, each atom is only partly surrounded by other atoms. On bringing an atom to the surface from the interior, bonds must be broken or distorted, and consequently there is an increase of energy. Surface free energy (F_s) is defined as the increase in free energy per unit area of new surface formed (erg cm^{-2}) and for liquids is equal to the force per unit length of surface tension (dyne cm^{-1}). The formation of a solid surface, a two-phase interface (solid-liquid, solid-solid, solid-vapor, liquid-vapor, liquid-liquid) or a single phase grain boundary also involves breaking or deforming interatomic bonds and gives rise to surface or interfacial free energies of the same order of magnitude as the corresponding liquid surface free energies.

Surface free energy can be determined either by a thermodynamic measurement or by a mechanical measurement of the surface force. For metallic and covalent materials, the surface free energy can be found by considering the number and energy of the bonds which must be broken

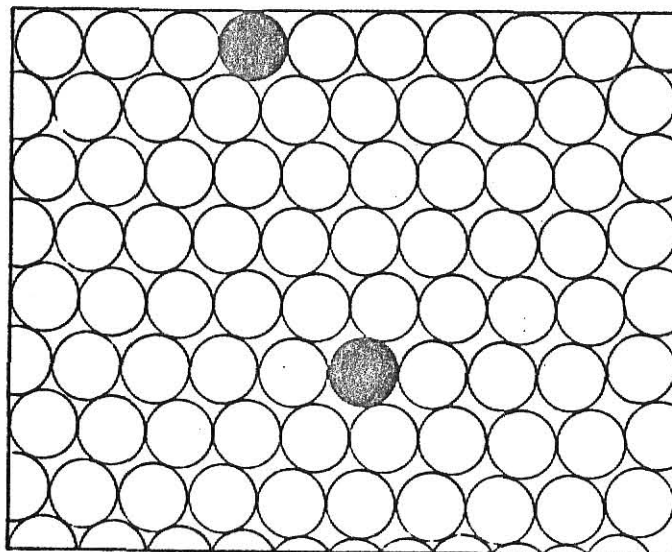


Fig. 7 . Cross Section of Solid Metal Illustrating the Difference in Surroundings of a Surface Atom and an Interior Atom.

to form the surface. Similarly, calculations of work done against the coulomb force lead to approximate values of surface free energy for ionic materials. In both cases, the surface free energy depends on crystallographic orientation. Direct measurement of surface free energy is possible by force equilibrium, if the phases are sufficiently mobile.

For solid metals and alloys, the values of surface and grain boundary free energies are at best difficult to measure accurately. Various experimental methods for determining the surface and grain boundary free energies of solid metals have been reviewed by Inman and Tipler (1963). Earlier reviews by Udin (1952), Hess (1952) and Fisher and Dunn (1952) describe additional techniques that have been employed. Empirical methods for determining surface free energy values of solid metals and alloys have been reviewed by Semenchenko (1960).

The concept of solid surface free energy must be carefully considered, particularly for an extension of this concept to solids at low temperatures. However, at high temperatures near the melting point where diffusion is rapid and grain growth occurs in polycrystalline metals and alloys, surface equilibrium will be restored during slow deformation. As a consequence, it would appear that the only experimentally feasible method of measuring approximate solid surface free energies would involve one in which these conditions are met. The only presently known method of this kind involves the "zero-creep technique" where a polycrystalline wire or thin foil is elongated at high temperature, and the grain boundaries intersecting the solid-vapor interface (the free surfaces) sustain equilibrium by the movement of atoms at the grain boundary interface.

Zero-Creep Techniques for the Measurement of Surface Free Energies

The zero-creep method of determining the surface free energy of solid metals and alloys was first used by Sawai and Nishida (1930) and Tamman and Boehme (1932), and modified by Udin et al. (1949), Udin (1951), Pranatis and Pound (1955), and Hondros (1965). The technique is predicated on the fact that very thin wires or foils contract when heated to temperatures close to the melting point because, for a large surface-to-volume ratio, the surface tension (or shrinkage force) will exceed the static stress associated with the weight of the wire or foil sample.

Zero-Creep of Polycrystalline Thin Foils

Grain boundaries in polycrystalline foils annealed under conditions to attain complete pseudoequilibrium will intersect both free surfaces of a thin sheet at right angles as illustrated in Fig. 8. The initial change in length of such thin foil specimens will be governed mainly by a redistribution of dislocations (Greenough, 1958), offsetting at inclined grain boundaries (Greenough, 1952) and orientation changes which reduce the specific grain boundaries (Herring, 1950). The linear extension or contraction of the specimen is generally assumed to be controlled by a Nabarro-Herring mechanism (Nabarro, 1948; Herring, 1950) where material transport is affected by a flow of vacancies from the grain boundaries to the external surfaces (solid-vapor interface) or vice versa. This so-called "vacancy creep" is particularly effective at high temperature where a metal or alloy foil specimen can be considered as an isotropic viscous medium.

If W_0 represents the load required to just balance the surface free energy or contractile forces, the condition for zero creep or zero

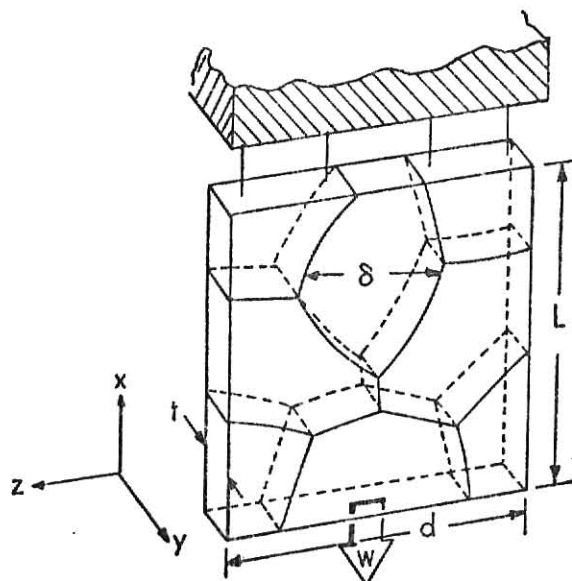


Fig. 8. Equilibrium Creep of Thin Foil Loaded in Tension by a Weight W .

strain rate in the x-direction in Fig. 8 is

$$W_o g = F_S d - \gamma_{gb} v(td/\delta) \quad (1)$$

where g is the gravitational constant, d is the foil width, t is the thickness, v is the Poisson's ratio for the condition of equilibrium, F_S is the surface free energy (solid-vapor interfacial energy), and γ_{gb} is the grain boundary free energy.

Hondros (1965) assumed that thin foil creep specimens did not change volume, and let $v = 0.5$; however, it is well known that v for most metals and alloys will vary from roughly 0.25 to 0.45. But since the average grain size of thin metal or alloy foils is ~ 0.5 mm, the specimen dimensions t and d may be manipulated so as to make the grain boundary term negligible when compared with the surface free energy term. Large grain size is not, however, a necessary condition for the use of Eq. (1) since the grain boundaries of a solid metal are always revealed as grooves during annealing at elevated temperature and each groove develops in such a manner so that the resultant of two surface free energies (F_S) and one grain boundary free energy (γ_{gb}) vanishes along the line of the grain boundary intersection as shown in Fig. 9. Chalmers et al. (1948) were among the first to describe this thermal grooving at the intersection of a solid-solid interface with the free (solid-vapor) surface as a condition of interfacial free energy minimization. Smith (1948) has shown that after a sufficiently long anneal, the dihedral angle, Ω_S , at the base of the groove is the characteristic of the surfaces and grain boundaries involved and that the size of the angle is determined by the equilibrium configuration of the surface and grain boundary free energies. At equilibrium, assuming that the surface free energy is independent of

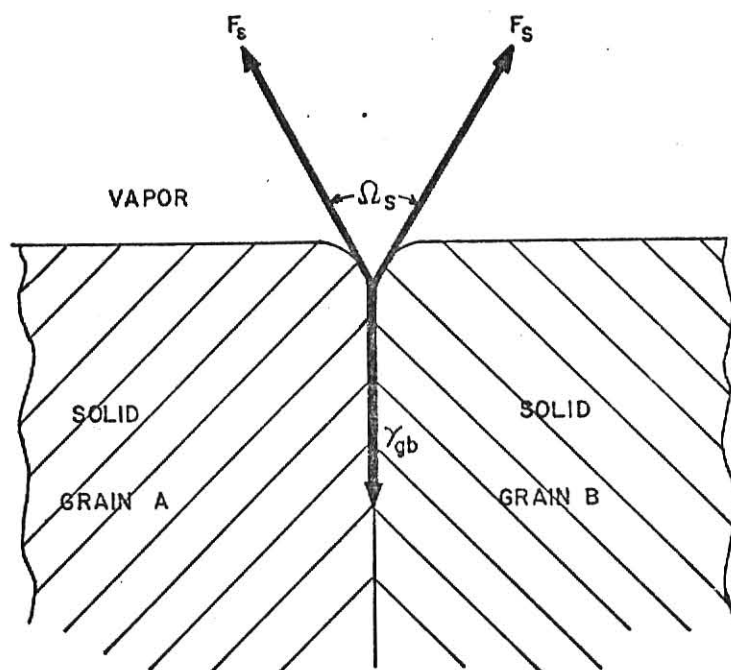


Fig. 9. Thermal Groove Profiles for Grain Boundary Surface Equilibria.

crystallographic orientation, the surface and grain boundary free energies are related by the expression

$$\gamma_{gb} = 2F_S \cos(\Omega_S/2) \quad (2)$$

Indeed, if the mean dihedral angle, Ω_S , is obtained by accurate observations of the groove angle at the intersection of the grain boundary with the free surfaces, substitution of Eq. (2) for γ_{gb} in Eq. (1) results in a single expression for the average surface free energy:

$$F_S = \frac{W_o g}{d[1 - 2\nu(t/\delta) \cos(\Omega_S/2)]} \quad (3)$$

It must be pointed out that the equilibrium condition described by Eq. (2) is valid only for symmetrical intersections, or approximations of such situations. As a consequence, annealed bulk metals and alloys may not exhibit symmetrical intersections where thermal equilibrium has not been established, in which case, additionally, large unbalanced torques may exist. Since Drechsler and Nicholas (1967) have found that surface free energy anisotropy decrease with increasing temperature, the neglect of torque contributions would be expected to be most valid near the melting point.

Zero-Creep of Polycrystalline Fine Wires

In many cases wire samples are preferred to foils because of the simpler stress system, and because the grain boundaries in fine wires are more easily described in the geometry of the system, with the result that the grain boundary free energy contribution can be more accurately determined. Under the conditions of zero-creep, the grain boundaries align themselves normal to the wire axis, forming a so-called "bamboo" structure (Fig.10). If a virtual work argument is considered, a fine

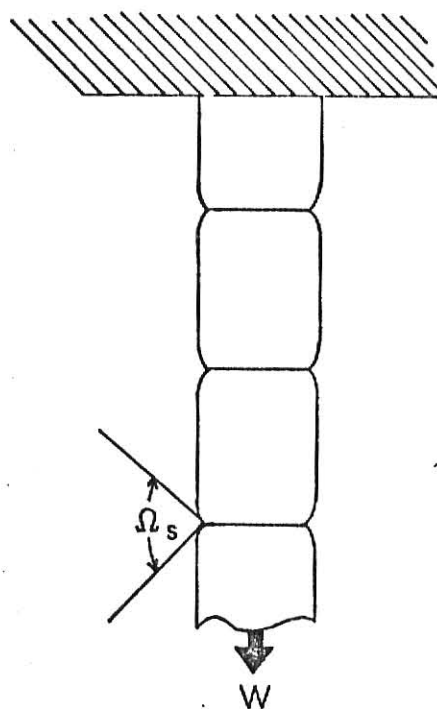


Fig. 10. Bamboo Structure of Fine Wires Crept at High Temperature.

wire of radius r carrying a balance load, W_o , then the condition for zero-creep (Udin, 1951) is

$$W_o = \pi r [F_S - \gamma_{gb} r (n/l)] \quad (4)$$

where n/l is the number of grains per unit length of fine wire.

Since fine wires are ideally suited to measuring the dihedral angle Ω_S , using the scanning electron microscope, Eq. (2) can be substituted for γ_{gb} in Eq. (4) to obtain

$$F_S = \frac{W_o}{\pi r [1 - 2(n/l)r \cos(\Omega_S/2)]} \quad (5)$$

Determination of Surface and Grain Boundary Free Energies from Fine Wires

Fine wires having diameters $<10^{-2}$ cm are prepared with various weights spot-welded (or attached in some other way) onto their free ends and hung in a cylindrical enclosure after being scribed or knotted intervals to act as gauge marks. The wires are annealed in a vacuum or inert gas atmosphere furnace at or above the test temperature for an initial period up to 20 hours, then they are cooled and straightened if necessary prior to measuring the distance between gauge marks. At this point, the grain boundaries are usually revealed by thermal etching. The thermal etched grooves developed during the anneal effectively anchor the grain boundaries and no further grain growth is found to occur during the subsequent creep test. This phenomenon, first noted by Udin (1952), suggests that the grains have recrystallized and grown to an equilibrium size and shape during the relatively short anneal. The wires are then heated and held at a temperature near the melting point of the metal for a predetermined length of time (about 50 to 200 hours). During this time, the weights on the wires tend to cause the wires to elongate, while the surface forces tend to cause the wires to shorten. The wires are cooled

and the change in length is determined. The creep of fine wires has been shown (Inman and Tipler, 1963; Inman, Mclean and Tipler, 1963; Allen, 1966) to be linearly controlled by a Nabarro-Herring mechanism. The strain of each wire is defined as

$$\epsilon = (L - L_0)/L_0 \quad (6)$$

where L_0 is the initial gauge length and L is the gauge length after creep anneal. The strain is then plotted against the effective weights determined by cutting the wire at the mid-point of the gauge length and weighing the wire and weight below this point. The tensile load for zero-creep, i.e., the balance load is determined graphically as shown in Fig.11 . The number of grains in each gauge length can be determined from the boundaries revealed by thermal etching since the grain boundaries ideally form a bamboo structure in which the wire is made up of a series of grains, the grain boundaries of which are perpendicular to the axis of the wire and the width of each grain equals the diameter of the wire. The value of dihedral angle can be obtained by several techniques but the most accurate measurements are done by using scanning (Murr, Horylev and Wong, 1971) or transmission electron microscope (Inman and Tipler, 1963; Inman, Mclean and Tipler, 1963; Greenough, 1965; Murr, Horylev and Wong, 1971). In these modes of analysis, the groove angles can be measured at the magnifications to ensure that the groove root is being considered at the point where the resolved grain boundary free energy and surface free energy vectors meet. All mean values of these experimental parameters are then substituted into Eq. (5) to obtain the value of the surface free energy of solid metal.

The value of grain boundary free energy can be determined directly after obtaining the value of surface free energy from Eq. (2),

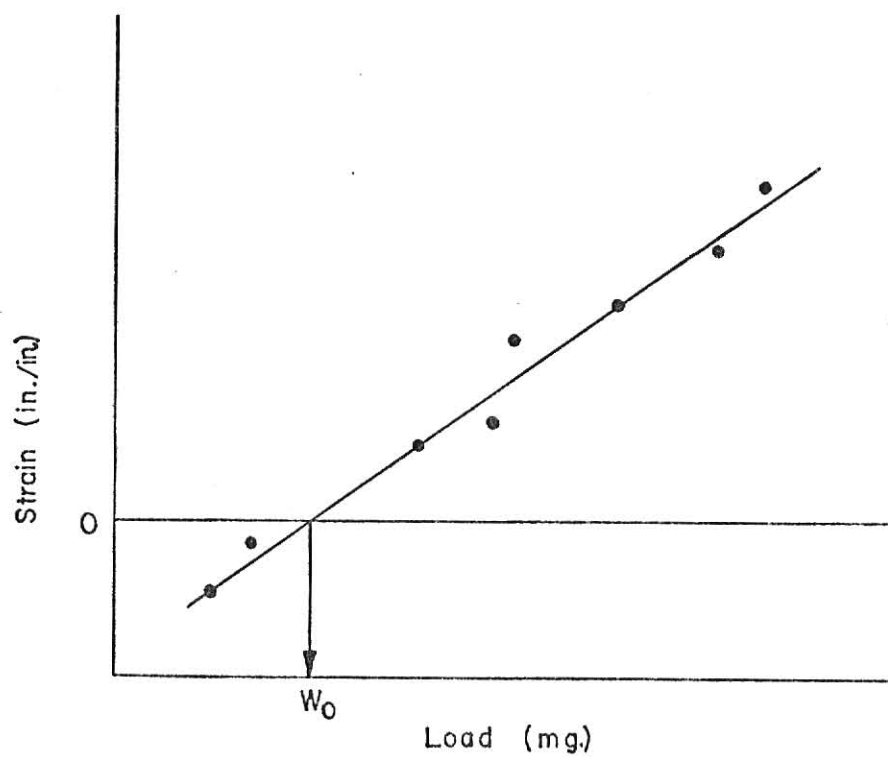


Fig. 11. Typical Load-Strain Curve for Zero-Creep Method with Least Square Line.

$$\gamma_{gb} = 2F_S \cos(\Omega_S/2).$$

Experimental evidence has accumulated showing that grain boundary free energy is generally about one-third of the surface free energy (Bailey and Watkins, 1950; Van Vlack, 1950; Greenough, 1950).

It should be noted that, because the wire surfaces consist of planes of many possible indices, the surface free energy measured by this method is an average value for the range of orientations in the surface of the wire. The value of grain boundary free energy is also an average, determined from the measurement of a large number of dihedral angles in each wire. The true dihedral angle is usually taken as the median of the distribution of a large number of angle measurements. Reigger and Van Vlack (1960) and Stickels and Hucke (1945) have shown that the median angle is very close to the true dihedral angle.

CHAPTER III

EXPERIMENTAL PROCEDURE

The results obtained in this research were determined by a two-step experimental procedure. First, the zero creep technique was applied to find the balance load which was determined by the change in the gauge length of the wires after annealing and the stress applied to the wires during the annealing heat treatment. Second, the equilibrium angles of thermal etching at grain boundaries were determined.

A high temperature vertical tube furnace, using resistance heating elements, as shown in Fig. 12, was used for the investigation. The temperature of the furnace was controlled by an indicating and controlling potentiometer using Pt/Pt - 13% Rh thermocouples. Prior to use, the furnace tube was heated for at least 24 hours while being evacuated at the anticipated testing temperature to remove any possible contaminants which might be given off during subsequent use. The furnace tubes were closed at one end with the open end connected to the vacuum and helium atmosphere system as shown in Fig. 13. The experiments were carried in the dried high purity helium atmosphere in order to avoid possible evaporation difficulties and prevent the oxidation of the metals. The prepurified helium gas used in the experiment was purchased with a specific dew point of -100°C and contained less than 15 p.p.m. each of neon and nitrogen and less than 22 p.p.m. of hydrogen. The gas was further purified by passing it through the microsiege trap to remove any water vapor present. Evacuation of the system was accomplished by the use of a mechanical vacuum pump.

The test metals obtained commercially were in the form of wire drawn down to 0.005 in. (0.0127 cm) in diameter. The compositions of pure titanium

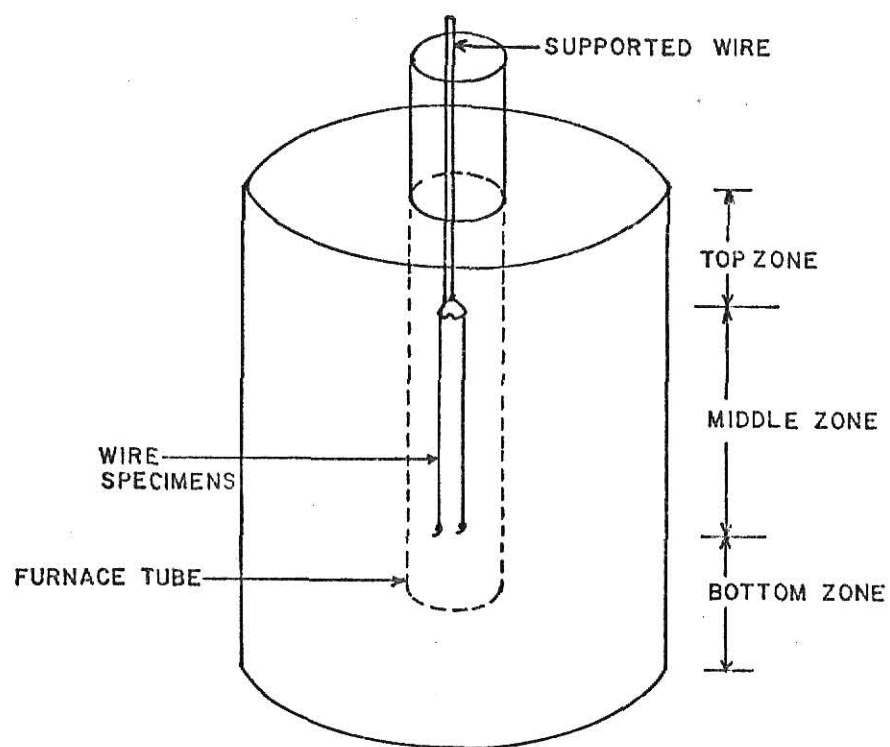


Fig. 12. Schematic Diagram of Furnace.

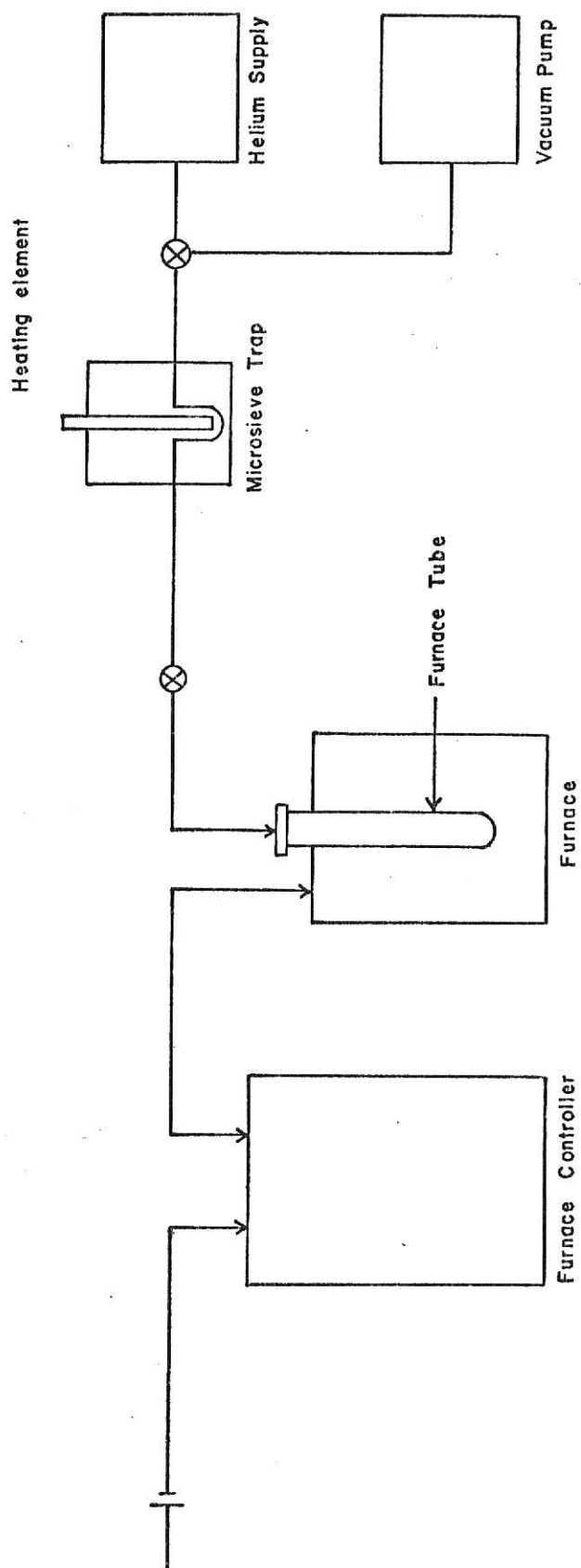


Fig. 13. Schematic Diagram of the Experimental Apparatus

wire used are given in Appendix A and those of Ti-6Al-4V alloy are shown in Table 2 .

The test specimens were cut from the reel, a loop was tied at one end from which the wire was hung in the furnace by means of a supported wire, and a weight which made of pure titanium metal was tied to the bottom of the test wire. Estimates of the balance load for zero creep, made from available data for the surface tension value for the liquid metal (Allen, 1963), were used to determine the amount of weight to be suspended from the wires. The wires were first washed with ethyl alcohol and acetone to dissolve any oils and dirt on them due to handling. They were then put into the furnace for the initial anneal about twenty hours at or near the test temperature in order to soften them prior to straightening, knotting, and initial measurement of the distance between gauge marks.

Prior to the initial anneal, the furnace chamber was flushed several times with dried high purity helium to insure that the wires would expose only to the desired atmosphere during the heat treatments. After the wires had cooled in the furnace, they were removed, straightened and knotted. Knots were tied less than 5 cm apart and several knots being tied in each wire to serve as gauge markers. The knots tied into the wires were found to sinter at the elevated temperatures used in the creep experiments and did not take part in the elongation or shrinkage of the wires. In most cases, the short time anneal was adequate to allow the grains to grow to the apparent equilibrium size and shape. The wires, when examined under a microscope, displayed the desired bamboo structure. After the creep anneals, the wires emerged from the furnace bright and ductile and they were believed to be free from any surface contamination.

Gauge length measurements were made on each wire before and after the creep anneals using a filar eyepiece micrometer microscope mounted for vertical measurement and capable of measuring to ± 0.00005 in. (0.000127 cm). The grains were observed to have retained the bamboo structure developed during the initial short time anneal and no apparent grain growth was noted. The number of grain boundaries per unit length (n/ℓ) were counted for each final gauge length measurement and the average value of n/ℓ was determined. Then, the strain for each portion of the wire was plotted against the effective weight determined by cutting the wire at the mid-point of the gauge length and weighing the wire and weight below this point. The balance load, W_0 , was determined as depicted in Figs. 14 and 15.

The grain boundary groove angles (Ω_S) were determined by scanning electron microscopy. Examination of the wires under the microscope showed that at 150 - 200X the grain boundary groove angles were clearly enough defined for direct measurement to within a standard deviation of $\pm 0.5^\circ$. The photographs of the groove angles obtained with the scanning electron microscope were enlarged prior to angle measurement. Numerous groove angles were photographed and measured for each wire. The median value for each test was taken to be the desired groove angle for that test.

Substitution of all these experimental parameters into the expressions

$$F_S = \frac{W_0}{\pi r [1 - 2r(n/\ell) \cos(\Omega_S/2)]}$$

and

$$\gamma_{gb} = 2F_S \cos(\Omega_S/2)$$

gave the absolute values of surface and grain boundary free energies of the wire specimens for each test.

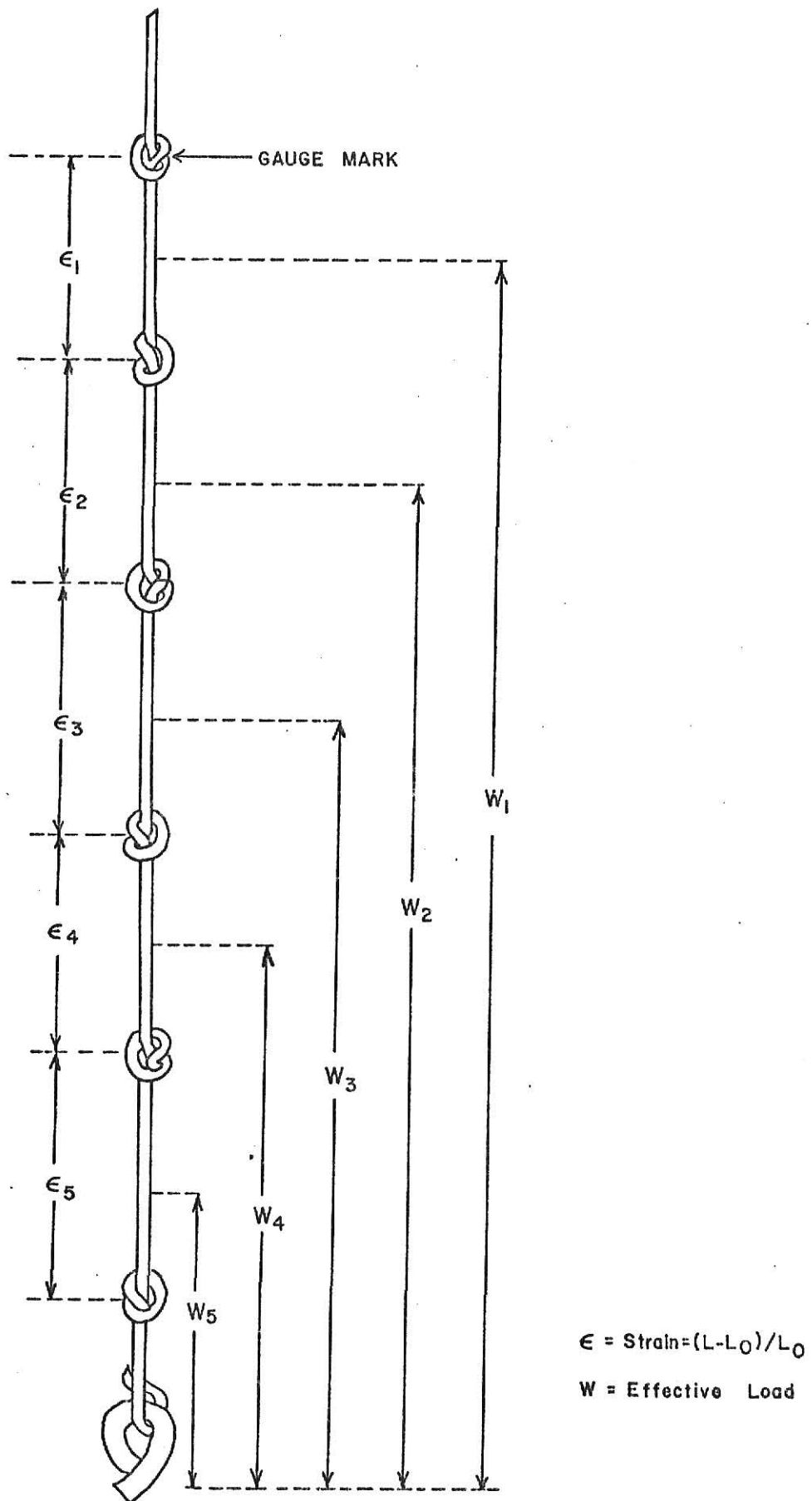


Fig. 14. Typical Wire Specimen Showing How the Effective Loads, W , and Strains, ϵ , are Determined.

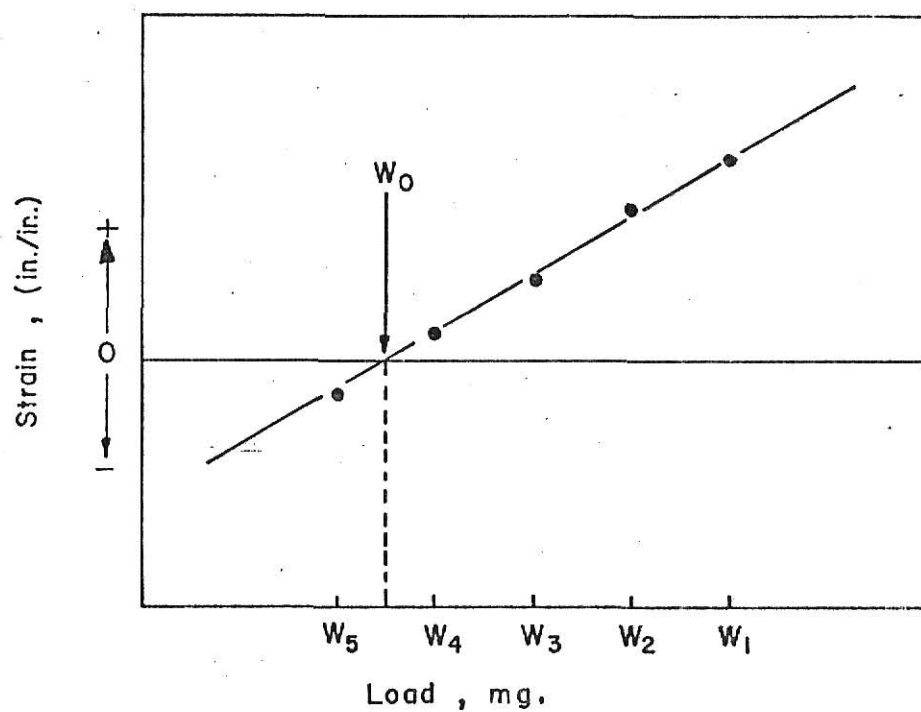


Fig. 15. Typical Plot of Data Obtained as Shown in Fig. 4 as Used to Determine the Load for Zero-Creep, W_0 .

CHAPTER IV

RESULTS

The determination of the surface and grain boundary free energy of pure titanium and Ti-6Al-4V alloy in a purified helium atmosphere were each conducted at four different temperatures. For pure titanium metal, the tests were performed at 2080, 2200, 2300 and 2400°F (1137.8, 1204.4, 1260 and 1315.6°C). The test temperatures for Ti-6Al-4V alloy were 2080, 2150, 2230 and 2345°F (1137.8, 1176.7, 1221.1 and 1285°C). The experimental data and results for pure titanium are given in Tables 3, 4, 5, 6 and summarized in Table 7. The experimental data and results for Ti-6Al-4V alloy are shown in Tables 8, 9, 10, 11 and summarized in Table 12.

Several wires (each wire being designated as Ti-1, Ti-2, etc. for pure titanium and Ti-4V-1, etc. for Ti-6Al-4V alloy) with several gauge lengths (6 to 9) were used to investigate the interfacial energies at each test temperature. Each of the gauge lengths in the wire was identified by a capital letter beginning from the top, as section A, B, C, etc.. The interfacial energies at each temperature reported in the Tables are considered to be the best values of the several tests which showed good reproducibility. In this study, the wire specimens were crept for a period of time, from about 23 to 115 hours. Using a vertical travelling micrometer microscope, gauge length measurements were made on each section of wire specimens before and after creep anneals. The resulting strains, reported as change in length per unit original length (in./in.), were plotted on linear coordinates versus the corresponding applied loads (mg.). A least square calculation was then used to determine the most probable critical load at zero strain. A typical

plot of these data for pure titanium at 2400°F is presented in Fig. 16. The critical load obtained for pure titanium on each test is in the range of 32.5 - 33.5 mg. and for Ti-6Al-4V alloy, it is in the range of 33.5 - 35.1 mg..

The actual number of grains per unit length for each section of the wire specimens was counted with the microscope during the final gauge length measurement. It was always possible to count the number of grains in each wire just after the initial short time anneal since the grains have recrystallized and grown to an equilibrium size and shape during this relatively short anneal. The average value for the number of grains per inch on each test of pure titanium is in the range of 179-190 and for Ti-6Al-4V alloy it is in the range of 181-188. The probable uncertainty in the average value was placed at ± 10 grains per inch to account both for the possible random error encountered in the grain counts and the deviation of the individual determinations from the average value. The reciprocal of the actual n/l and the average n/l were then taken to give the actual length of a grain and the average grain length. As is shown in the Table, the average grain length of both pure titanium and Ti-6Al-4V alloy was almost the same, lying approximately from 5.3 to 5.6×10^{-3} inch (1.35 to 1.42×10^{-2} cm.).

The thermally etched groove at the intersection of the grain boundary with the surface of the wire which was formed during the creep anneal was distinctly visible. Examination of the wire specimens by using scanning electron microscopy indicated that the wires had developed the expected bamboo structure and the grain boundary grooves are evident, as readily apparent in Figs. 17 and 18. Direct angle measurements were made from the enlarged photographic prints and the average dihedral angle was determined

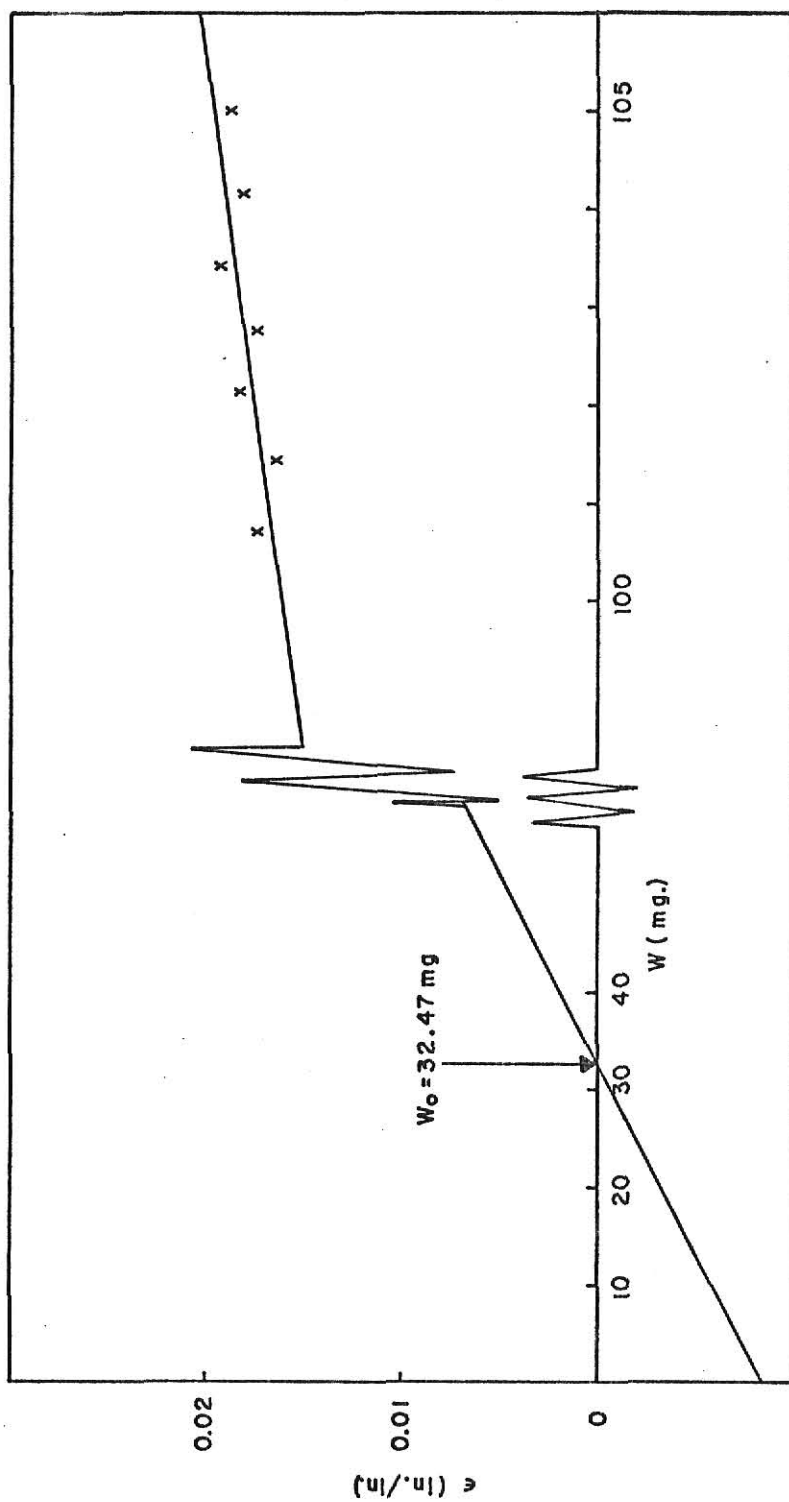


Fig. 16. The Typical Experimental Load-Strain Curve of Pure Titanium at 2400°F.

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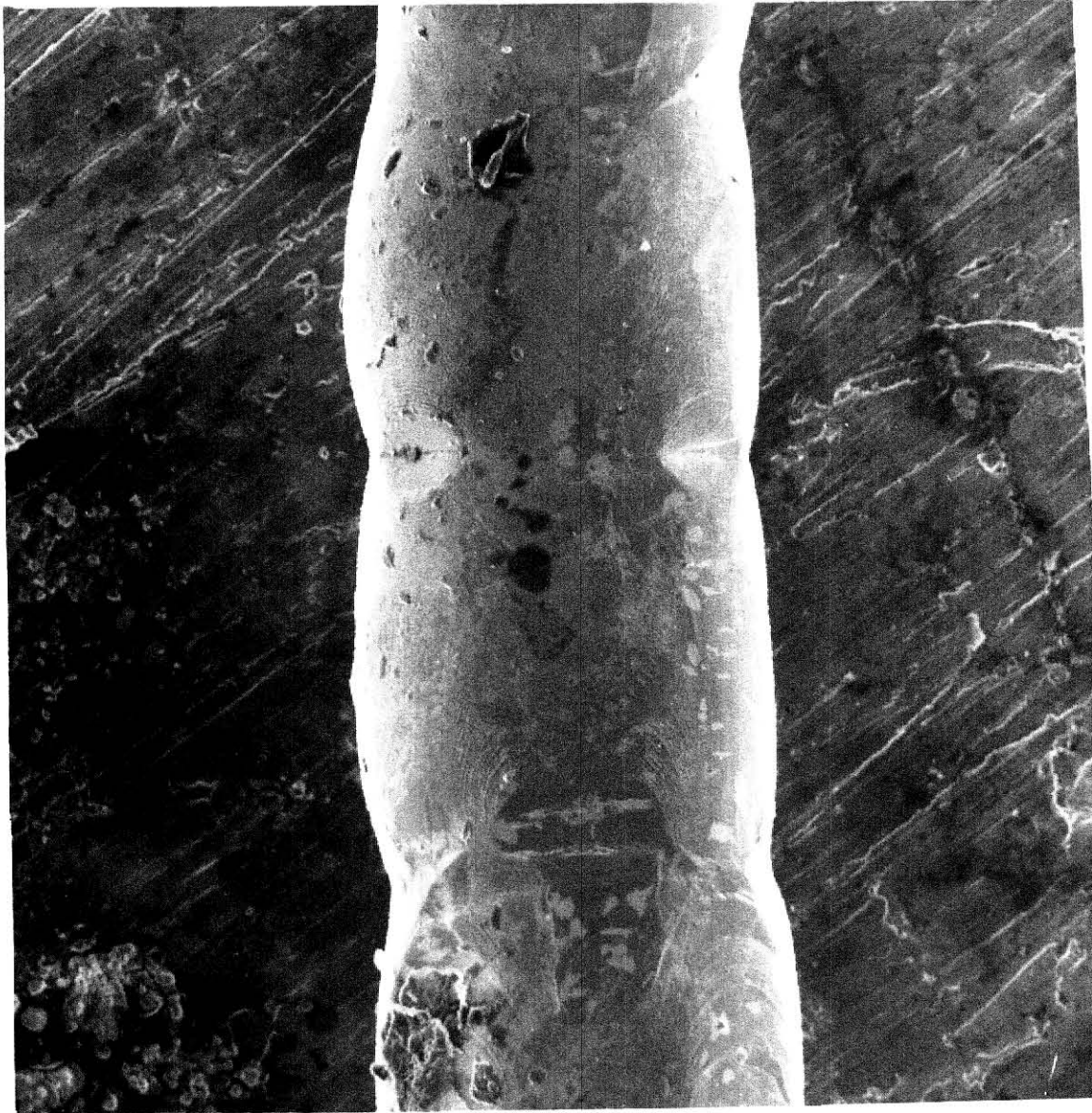


Fig. 17. Typical Appearance of Segments of the Wires After Creep in He Atmosphere Showing the Thermally Etched Grain Boundary Grooves in Pure Titanium.

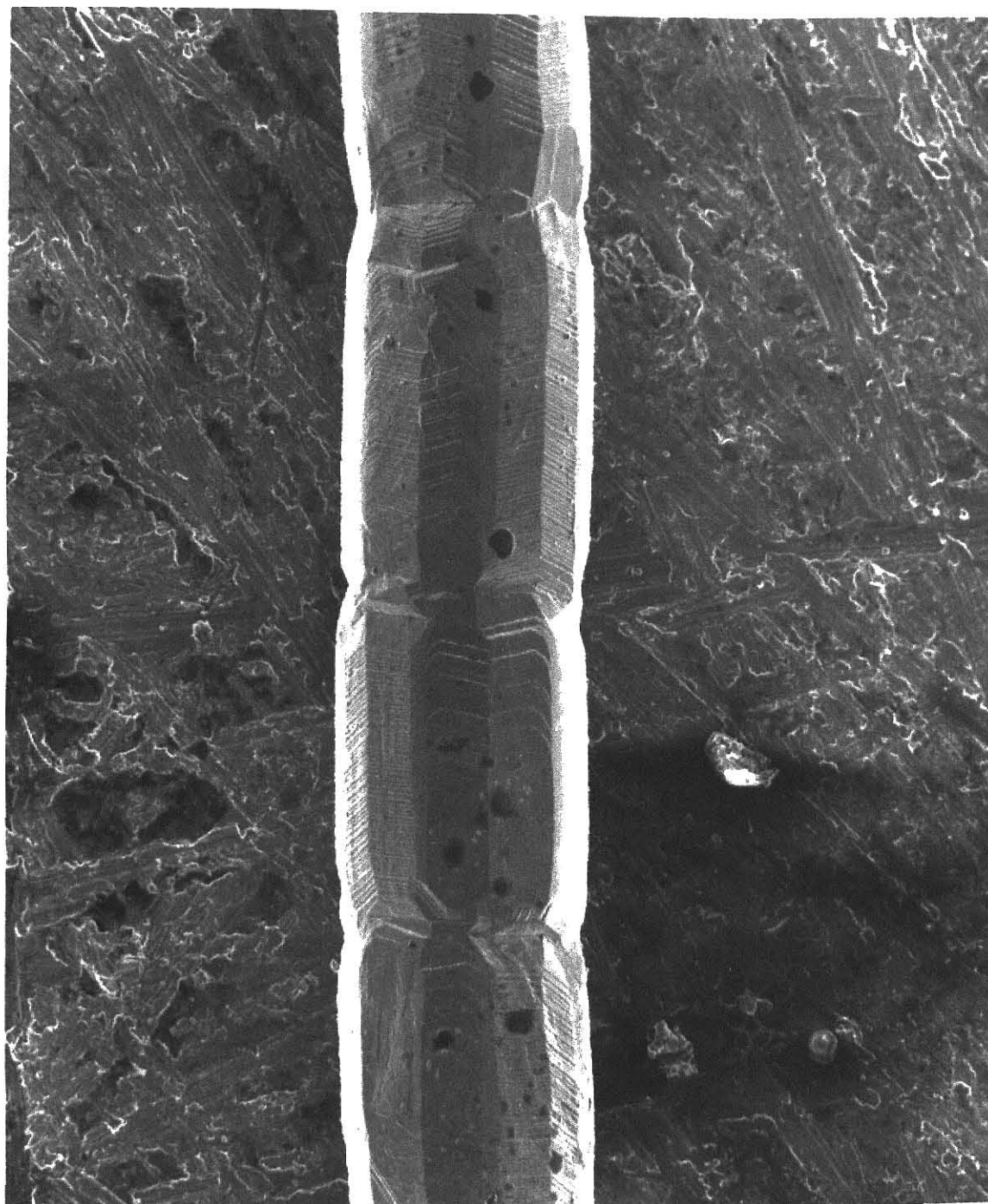


Fig. 18. Typical Appearance of the Segments of the Wires After Creep in He Atmosphere Showing the Thermally Etched Grain Boundary Grooves in Ti-6Al-4V.

from the many separate angle measurements made on the wire specimens on each test. The dihedral angle values thus obtained had an uncertainty of the order of $\pm 2.5^\circ$ which was believed to be due primarily to statistical error. The range of the dihedral angles for both pure titanium and Ti-6Al-4V alloy are also reported in the Table taken from the lowest to the highest value of the measured angles.

The surface free energy values reported in all the tests were computed from Eq. (5),

$$F_s = \frac{W_o}{\pi r[1 - 2r(n/\ell)\cos(\Omega_s/2)]}$$

Using the value of surface free energy thus computed, the corresponding grain boundary free energy and the ratio of grain boundary to surface free energy were determined. The probable error of the computed values of the surface and grain boundary free energy was determined from the uncertainties in the terms of the above equation. The error in the computed values was found to be generally in the range of ± 5 -10% (standard deviation).

The variation of surface free energy and grain boundary free energy with temperature for pure titanium is illustrated in Figs. 19 and 20 and that for Ti-6Al-4V alloy is shown in Figs. 21 and 22. The temperature coefficients of surface and grain boundary free energy were obtained by the method of least squares. For pure titanium, the temperature coefficient of surface free energy is $-0.435 \text{ ergs/cm}^2^\circ\text{C}$ and the temperature coefficient of grain boundary free energy is $-0.65 \text{ ergs/cm}^2^\circ\text{C}$. For Ti-6Al-4V alloy, the temperature coefficient of surface free energy and grain boundary free energy is $-0.443 \text{ ergs/cm}^2^\circ\text{C}$ and $-0.10 \text{ ergs/cm}^2^\circ\text{C}$, respectively.

Table 3. Experimental Data and Results of Surface and Grain Boundary Free Energy Measurement for Pure Titanium at 2080°F (1137.80°C)*

Wire No.	Actual a/ℓ	Actual ℓ ($\times 10^{-3}$ in.)**	Average n/ℓ	Average ℓ ($\times 10^{-3}$ in.) and range	Applied load, W (mg.)	Strain ϵ (in./in.)	Critical load, W_0 (mg.)	Average angle, θ_S and range	Surface free energy, γ_S (ergs/cm ²)	Grain boundary free energy, γ_{gb} (ergs/cm ²)	γ_{gb}/γ_S
Ti-82			185.07	5.403			33.11	157.83	1980.23	761.48	0.385
A	189.52	5.276		(5.276-5.647)	129.55	0.00933519		(149-166)			
B	186.18	5.371			127.65	0.00883210					
C	189.17	5.286			125.83	0.00679234					
D	187.60	5.330			124.20	0.00943002					
E	182.49	5.480			122.51	0.00803366					
F	177.09	5.647			120.69	0.00847754					
G	183.47	5.450			118.74	0.00741559					

*Creep time: 96 hrs.

**1 inch = $2.54 \times 10^4 \mu\text{m}$

Table 4. Experimental Data and Results of Surface and Grain Boundary Free Energy Measurement for Pure Titanium at 2200°F (1204.4°C)*

Wire No.	Actual n/λ	Actual λ ($\times 10^{-3}$ in.)**	Average n/λ	Average λ ($\times 10^{-3}$ in.) and range	Applied load, W (mg.)	Strain ϵ (in./in.)	Critical load, W_0 (mg.)	Average angle, Ω_S and range	Surface free energy, F_S (ergs/cm ²)	Grain boundary free energy, γ_{gb} (ergs/cm ²)	γ_{gb}/F_S
Ti-81			187.04	5.346			32.60	156.95	1970.99	787.61	0.399
A	183.40	5.452		(5.164-5.496)	132.74	0.06244283		(148-166)			
B	190.02	5.263			130.82	0.05921054					
C	181.95	5.496			129.04	0.03889341					
D	184.51	5.420			127.22	0.05127982					
E	193.65	5.164			125.43	0.05503312					
F	192.43	5.197			123.49	0.05541657					
G	186.47	5.363			121.46	0.03119037					
H	182.45	5.481			119.42	0.04705262					
I	188.52	5.304			117.29	0.04000141					

*Creep time: 96 hrs.

** 1 inch = $2.54 \times 10^4 \mu\text{m}$

Table 5. Experimental Data and Results of Surface and Grain Boundary Free Energy Measurement for Pure Titanium at 2300°F (1260°C)*

Wire No.	Actual n/l	Actual ℓ ($\times 10^{-3}$ in.)**	Average n/l	Average $\ell(\times 10^{-3}$ in.) and range	Applied load, W (mg.)	Strain, ϵ (in./in.)	Critical load, W_0 (mg.)	Average angle, Ω_S and range	Surface free energy, F_S (ergs/cm ²)	Grain boundary free energy, γ_{gb} (ergs/cm ²)	γ_{gb}/F_S
Ti-54			189.54	5.276			33.46	160.26	1964.34	673.41	0.343
A	180.84	5.530		(5.077-5.605)	138.81	0.05923107		(140-169)			
B	178.42	5.605			136.44	0.04065625					
C	194.22	5.149			134.40	0.02047782					
D	187.56	5.332			132.65	0.03725602					
E	190.91	5.238			130.74	0.05527599					
F	188.63	5.301			128.69	0.03895430					
G	196.97	5.077			126.85	0.02442041					

*Creep time: 98 3/4 hrs.

**1 inch = 2.54×10^4 μ m

Table 6. Experimental Data and Results of Surface and Grain Boundary Free Energy Measurement for Pure Titanium at 2400°F (1315.60°C)*

Wire No.	Actual n/λ	Actual λ ($\times 10^{-3}$ in.)**	Average n/λ	Average λ ($\times 10^{-3}$ in.) and range	Applied load, W (mg.)	Strain, ϵ (in./in.)	Critical load, W_o (mg.)	Average angle, θ_s and range	Surface free energy, γ_s (ergs/cm ²)	Grain boundary free energy, γ_{gb} (ergs/cm ²)	γ_{gb}/γ_s
Ti-17			178.63	5.598			32.47	159.66	1895.35	669.32	0.353
A	179.90	5.559		(5.292-6.131)	105.99	0.02012350		(146.5-169)			
B	163.47	6.117			105.02	0.01864432					
C	163.10	6.131			104.21	0.01817233					
D	177.23	5.641			103.45	0.01911082					
E	188.98	5.292			102.79	0.01748422					
F	187.89	5.322			102.18	0.01812136					
G	177.43	5.636			101.46	0.01636421					
H	182.74	5.472			100.71	0.01705390					

*Creep time: 23 1/2 hrs.

**1 inch = 2.54×10^4 μ m

Table 7. Summary of the Experimental Data and Results of Surface and Grain Boundary Free Energy for Pure Titanium

Temperature	°F	°C	Wire no.	Creep time (hrs.)	Average $n/2$	Mean grain length, $\bar{L}$ ($\times 10^{-3}$ in.)	Average angle, $\bar{\alpha}_s$	Range of angle	Critical load, W_0 (mg.)	Surface free energy, F_s (ergs/cm ²)	Grain boundary free energy, γ_{gb} (ergs/cm ²)	γ_{gb}/F_s
2080	1137.8		Ti-88	96	185.07	5.403	157.83	149-166	33.11	1980.23	761.48	0.385
2200	1204.4		Ti-81	96	187.04	5.346	156.95	148-166	32.60	1970.99	787.61	0.399
2300	1260.0		Ti-54	98 3/4	189.54	5.276	160.26	140-169	33.46	1964.34	673.41	0.343
2400	1315.6		Ti-17	23 1/2	178.63	5.598	159.66	146.5-169	32.47	1895.35	669.32	0.353

Table 8. Experimental Data and Results of Surface and Grain Boundary Free Energy Measurement for Ti-6Al-4V Alloy at 2080° F (1137.8° C)*

Wire No.	Actual n/%	Actual ℓ ($\times 10^{-3}$ in.)**	Average n/ ℓ	Average λ ($\times 10^{-3}$ in.) and range	Applied load, W (mg.)	Strain, ϵ (in./in.)	Critical load, W_0 (mg.)	Average angle, Ω_S and range	Surface free energy, F_S (ergs/cm ²)	Grain boundary free energy, γ_{gb} (ergs/cm ²)	γ_{gb}/F_S
Ti-4V-51			182.27	5.486			35.12	157.71	2096.09	810.31	0.387
A	181.59	5.507		(5.296-5.762)	114.71	0.04562178		(146.5-166)			
B	173.55	5.762			113.40	0.04139241					
C	187.96	5.320			111.97	0.02034538					
D	186.39	5.365			110.60	0.03244501					
E	176.81	5.656			109.31	0.04166004					
F	188.83	5.296			108.01	0.03565710					
G	177.49	5.634			106.59	0.03436159					
H	185.53	5.390			105.24	0.03371250					

*Creep time: 60 hrs.

**1 inch = $2.54 \times 10^4 \mu\text{m}$

Table 9. Experimental Data and Results of Surface and Grain Boundary Free Energy Measurement for Ti-6Al-4V Alloy at 2150°F (1176.7°C)*

Wire no.	Actual $n/\%$	Actual ℓ ($\times 10^{-3}$ in.)**	Average $n/\%$	Average ℓ ($\times 10^{-3}$ in.) and range	Applied load, W (mg.)	Strain, ϵ (in./in.)	Critical load, W_0 (mg.)	Average angle, Ω_S and range	Surface free energy, γ_S (ergs/cm ²)	Grain boundary free energy, γ_{gb} (ergs/cm ²)	γ_{gb}/γ_S
Ti-4V-48			182.28	5.486			34.37	154.89	2107.43	916.23	0.435
A	179.89	5.559		(5.351-5.677)	141.36	0.0590575		(147-165.5)			
B	176.15	5.677			140.23	0.07067982					
C	185.83	5.381			139.19	0.06668460					
D	183.51	5.449			137.96	0.03675460					
E	183.06	5.463			136.75	0.07868566					
F	183.65	5.445			135.38	0.03881880					
G	180.75	5.533			134.03	0.07659511					
H	180.77	5.532			132.85	0.07533190					
I	186.87	5.351			131.46	0.07036190					

* Creep time: 96 hrs.

** 1 inch = $2.54 \times 10^4 \mu\text{m}$

Table 10. Experimental Data and Results of Surface and Grain Boundary Free Energy Measurement for Ti-6Al-4V Alloy at 2230°F (1221.1°C)*

Wire No.	Actual $n/2$	Actual ℓ ($\times 10^{-3}$ in.)**	Average $n/2$	Average ℓ ($\times 10^{-3}$ in.) and range	Applied load, W (mg.)	Strain, ϵ (in./in.)	Critical load, W_0 (mg.)	Average angle, θ_S and range	Surface free energy, F_S (ergs/cm ²)	Grain boundary free energy, γ_{gb} (ergs/cm ²)	γ_{gb}/F_S
Ti-4V-22			181.41	5.512			33.37	156.60	2010.41	815.38	0.406
A	***			(5.327-5.634)				(147-168)			
B	177.60	5.631			83.85	0.06494650					
C	185.00	5.405			82.78	0.05061891					
D	179.50	5.571			81.64	0.03432311					
E	183.71	5.443			80.34	0.05493758					
F	180.62	5.537			79.11	0.05843341					
G	180.00	5.556			77.96	0.04864370					
H	181.07	5.523			76.65	0.05137824					
I	177.50	5.634			75.24	0.04970428					
J	187.73	5.327			73.89	0.04167283					

* Creep time: 115 hrs.

** 1 inch = $2.54 \times 10^4 \mu\text{m}$

*** Accidental damage

Table 11. Experimental Data and Results of Surface and Grain Boundary Free Energy Measurement for Ti-6Al-4V Alloy at 2345°F (1285°C)*

Wire No.	Actual n/ℓ	Actual ℓ ($\times 10^{-3}$ in.)**	Average n/ℓ	Average ℓ ($\times 10^{-3}$ in.) and range	Applied load, W (mg.)	Strain, ϵ (in./in.)	Critical load, W_0 (mg.)	Average angle, α_s and range	Surface free energy, F_s (ergs/cm ²)	Grain boundary free energy, γ_{gb} (ergs/cm ²)	γ_{gb}/F_s
Ti-4V-53			187.47	5.334			33.78	156.59	2050.83	832.10	0.406
A	184.88	5.409		(5.219-5.495)	104.50	0.08901861		(148-168.5)			
B	191.26	5.229			103.37	0.07714095					
C	189.71	5.271			102.27	0.08843451					
D	181.98	5.495			101.13	0.08415299					
E	189.99	5.263			99.90	0.07068742					
F	182.27	5.486			98.58	0.07183108					
G	188.09	5.317			97.27	0.06906802					
H	191.61	5.219			95.96	0.05278334					

* Creep time: 60 hrs.

** 1 inch = $2.54 \times 10^4 \mu\text{m}$

Table 12. Summary of the Experimental Data and Results of Surface and Grain Boundary Free Energy for Ti-6Al-4V Alloy

Temperature		Wire No.	Creep time (hrs.)	Average n/λ	Mean grain length, λ ($\times 10^{-3}$ in.)	Average angle, θ_S	Range of angle	Critical load, K_c (mg.) ⁰	Surface free energy, F_S (ergs/cm ²)	Grain boundary free energy, γ_{gb} (ergs/cm ²)	γ_{gb}/F_S
$^{\circ}$ F	$^{\circ}$ C										
2080	1137.8	Ti-4V-51	60	182.27	5.486	157.71	146.5-166	35.12	2096.09	810.31	0.387
2150	1176.7	Ti-4V-48	96	182.28	5.486	154.89	147-165.5	34.37	2107.43	916.23	0.435
2230	1221.1	Ti-4V-22	115	181.41	5.512	156.60	147-168	33.37	2010.41	815.38	0.406
2345	1285.0	Ti-4V-53	60	187.47	5.334	156.59	148-168.5	33.78	2050.83	832.10	0.406

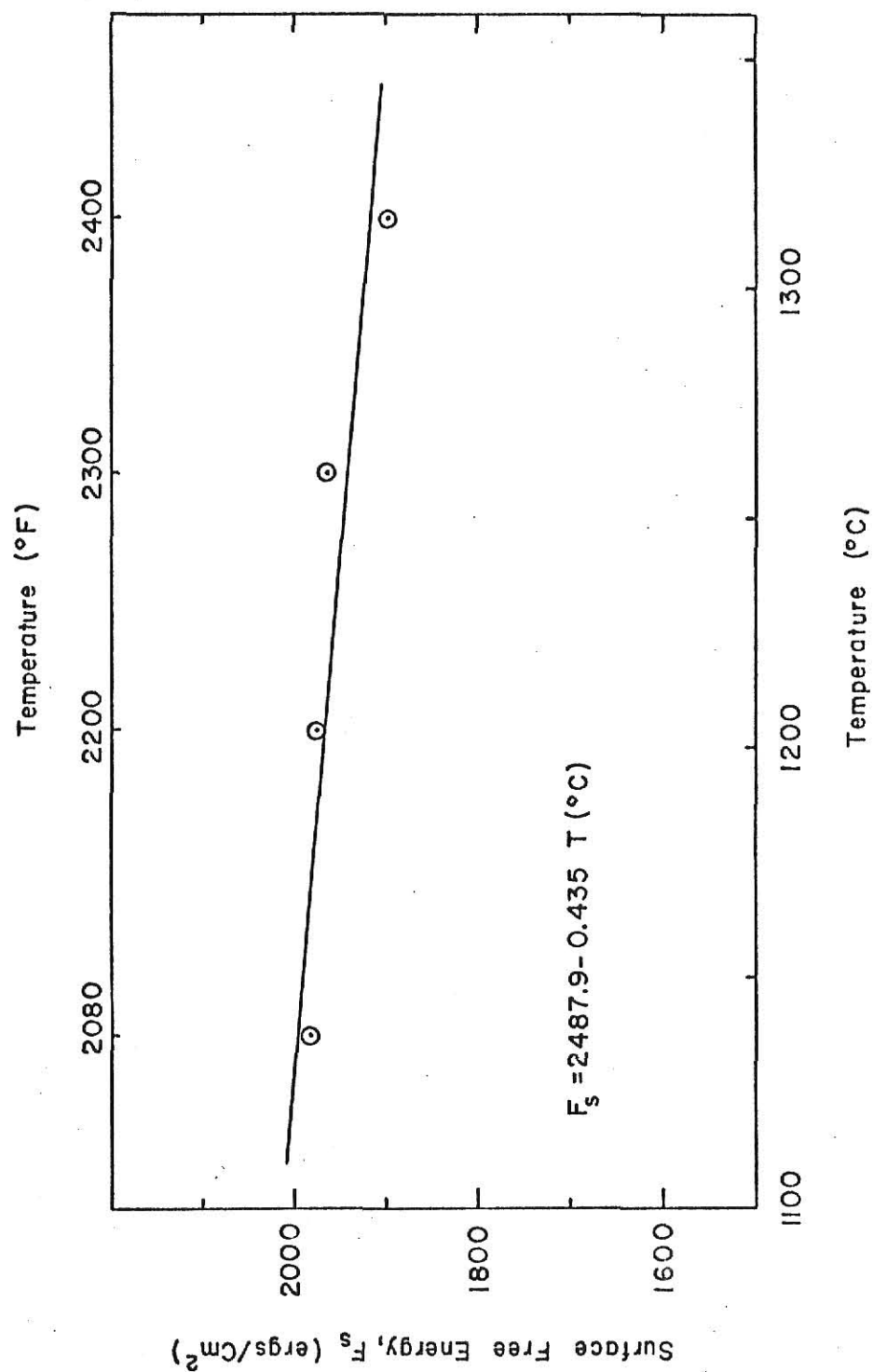


Fig. 19. The Temperature Dependence of Surface Free Energy of Pure Titanium.

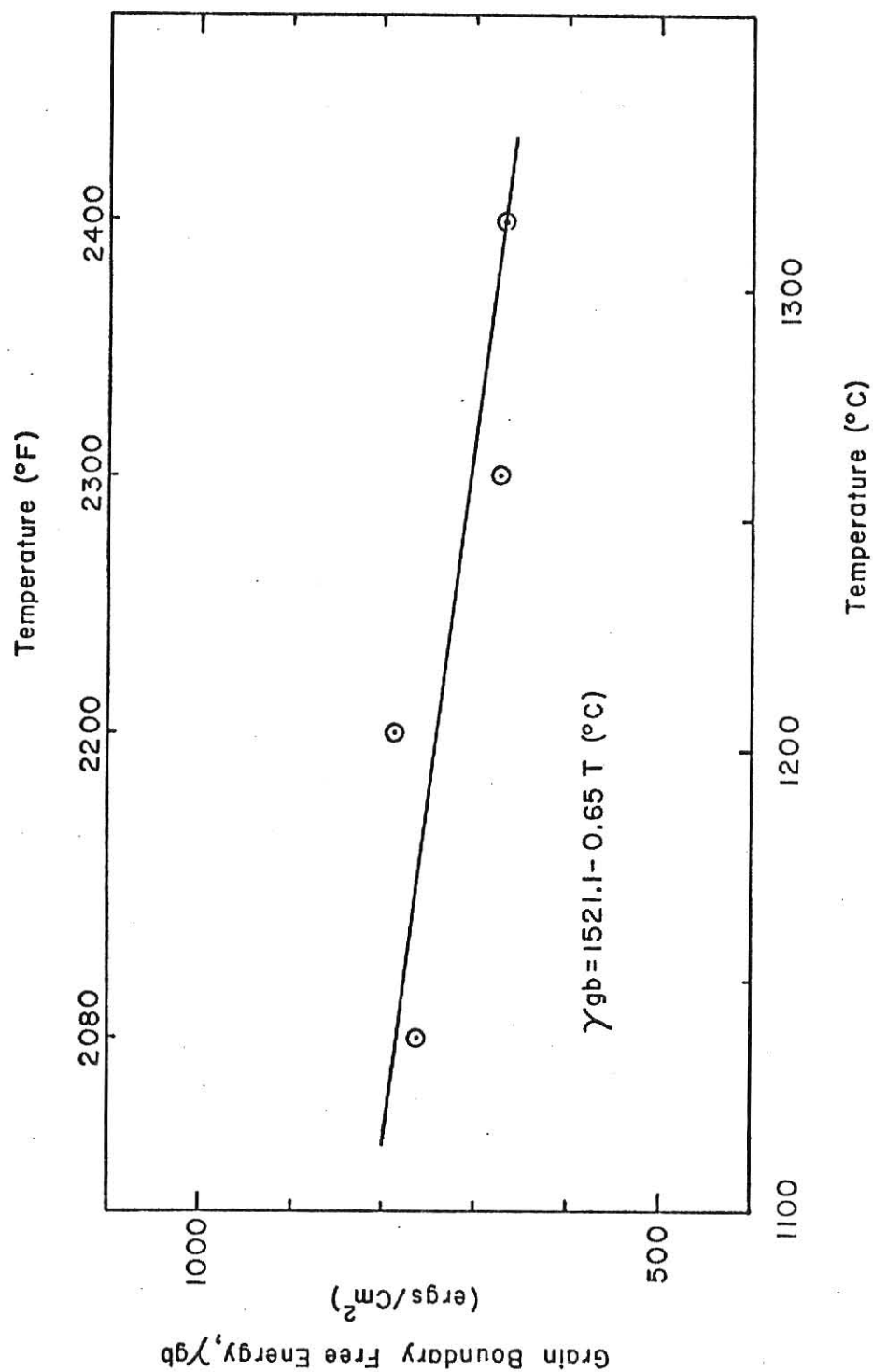


Fig. 20. The Temperature Dependence of Grain Boundary Free Energy of Pure Titanium.

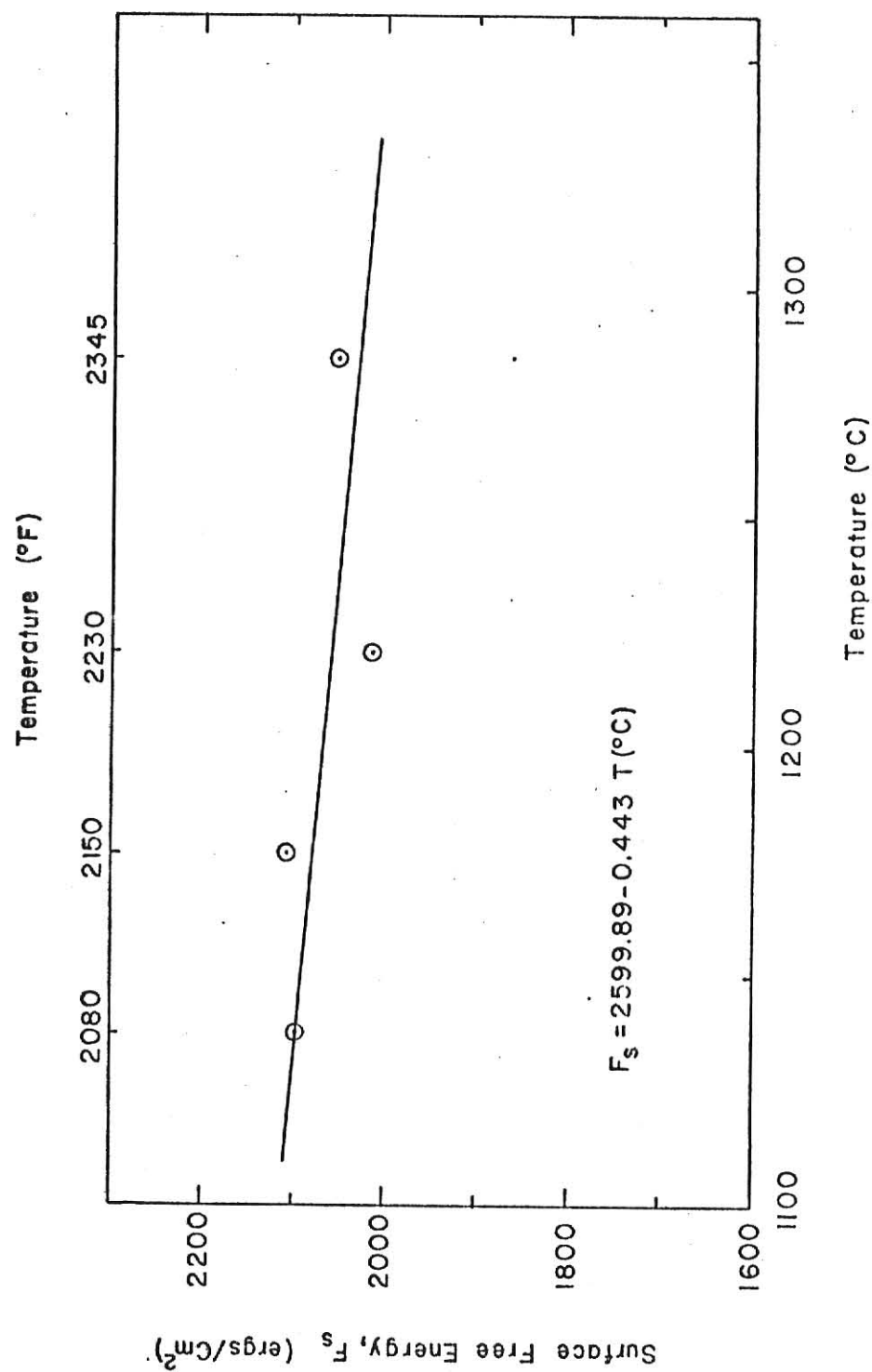


Fig. 21. The Temperature Dependence of Surface Free Energy of Ti-6Al-4V Alloy.

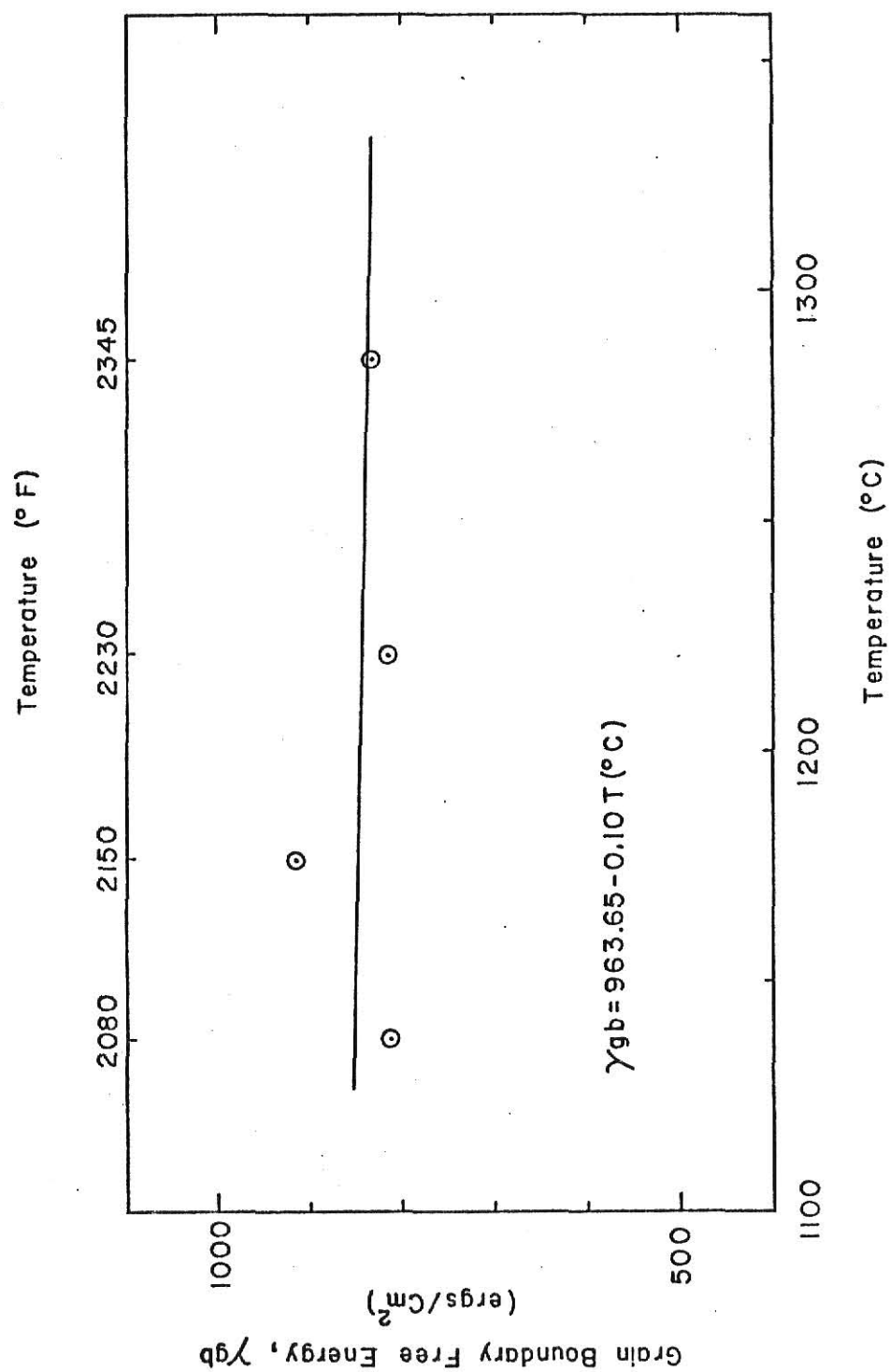


Fig. 22. The Temperature Dependence of Grain Boundary Free Energy of Ti-6Al-4V Alloy.

CHAPTER V

DISCUSSION

1) SURFACE AND GRAIN BOUNDARY FREE ENERGIES OF PURE TITANIUM AND Ti-6Al-4V ALLOY

Since there is no published experimental data on the interfacial free energies of Ti-6Al-4V alloy, comparison of the results reported here to other work is impossible. Most of the discussion of the interfacial free energy values, therefore, concerns the results found for pure titanium. Study of surface free energy at various temperatures shows that the surface free energy of pure metal increases with decreasing temperature when using inert atmospheres. This is in agreement with earlier investigations reported in the literature. Measurements of surface free energies for solid metals have been less extensive than surface tension measurements for liquids. Because of the critical conditions necessary to carry out zero-creep experiments, and the precision required in measuring variations in surface free energy with temperatures near the melting point in the solid state, very little experimental data on the surface free energy of solid titanium has been reported. Only one is found in the literature, an investigation of the surface free energy value for solid pure titanium by Kostikov et al. (1968). Their report is a very brief account and defies thorough comparison. In order to confirm the results found in this study, the value of surface free energy has been corrected and compared with earlier published surface tension of liquid pure titanium. Using the temperature coefficient of the surface free energy for pure titanium, an extrapolation to the melting point temperature (1730°C) is made and estimated value of about 1735 ergs/cm² is obtained. Evidence from a few direct

measurements and from nucleation studies (Adamson, 1976) suggests that a solid near its melting point generally has the surface free energy 10 to 20% higher than the liquid - about in the proportion of the heat of sublimation to that of liquid vaporization. Assuming that the surface free energy of solid pure titanium is 10% higher than that of liquid titanium at its melting point, the estimated value of surface tension for liquid pure titanium for this work is found to be 1560 ergs/cm^2 . The best value of the published surface tension for liquid pure titanium at its melting point done in vacuum is reported as $1650 \pm 50 \text{ ergs/cm}^2$ by Allen (1963). In his study, precautions were taken to avoid the effects of surface contamination and surface-active impurities. An earlier reported surface tension value found by Peterson et al. (1958) appears to be too low due to the surface contamination and impurity effect. Although Allen's study was done in vacuum, comparison of his result with the value found in this study in a helium atmosphere shows good agreement when corrections for decreasing temperature and solidification are made. The small difference (which is less than 10%) between the value found in this study and that of Allen is believed to result from the difference in composition of the titanium used in the two studies.

Kostikov et al. (1968) reported the value of surface free energy, for solid pure titanium using a zero-creep technique in vacuum as 1700 ergs/cm^2 at 1600°C . By extrapolation, using the temperature coefficient of surface free energy, an estimated value of 1790 ergs/cm^2 is obtained for this work. Comparison of this value with that of Kostikov et al. shows that their value may be low owing to surface contamination and/or impurity effects. The brevity of their report limits adequate comparison.

For the value of grain boundary free energies for pure titanium, no information is available for the comparison. Bailey and Watkins (1950), Van Vlack (1950) and Greenough (1950) found that grain boundary free energy is generally about one-third of surface free energy for pure metals. The grain boundary free energy values for pure titanium obtained in this study are in the range of 670-790 ergs/cm² and the values of γ_{gb}/F_S are in the range of 0.34-0.40 over the temperature range 1138-1316°C. Comparison of these results with those published values of grain boundary free energies for other pure metals shows the right range of grain boundary free energies obtained and the values of γ_{gb}/F_S also give good agreement with reported studies.

Comparison of the interfacial free energies for the Ti-6Al-4V alloy with those of pure titanium is given in Table 13. As is to be seen, the values of surface and grain boundary free energies of the Ti-6Al-4V alloy are generally higher than those of pure titanium. The difference in surface free energy between these two materials is about 100 ergs/cm². Since no values of the interfacial free energies of the Ti-6Al-4V alloy have been reported, no comparison of the values found in this study can be made. However, the surface and grain boundary free energies for the Ti-6Al-4V alloy obtained appear to be reasonable when compared to the values for pure titanium. Murr (1975) has plotted the value of surface free energy of solid metals and alloys versus the modulus of elasticity at 0.9 T_m (T_m = melting point temperature) as depicted in Fig. 23. It can be approximated from this figure that the modulus of elasticity almost linearly depends on the surface free energy value for solid metals and alloys. Pure titanium metal has a relatively low elastic constant and

Table 13. Comparison of the Surface and Grain Boundary Free Energy Obtained by the Least Square Method of Pure Titanium With Ti-6Al-4V Alloy at Various Temperatures.

Temperature, °F	2080	2200	2300	2400
<u>Pure titanium</u>				
F_S , ergs/cm ²	1993	1964	1940	1916
γ_{gb} , ergs/cm ²	783	739	703	667
γ_{gb}/F_S	0.393	0.376	0.362	0.348
<u>Ti-6Al-4V alloy</u>				
F_S , ergs/cm ²	2096	2066	2042	2017
γ_{gb} , ergs/cm ²	850	846	842	835
γ_{gb}/F_S	0.406	0.409	0.412	0.414

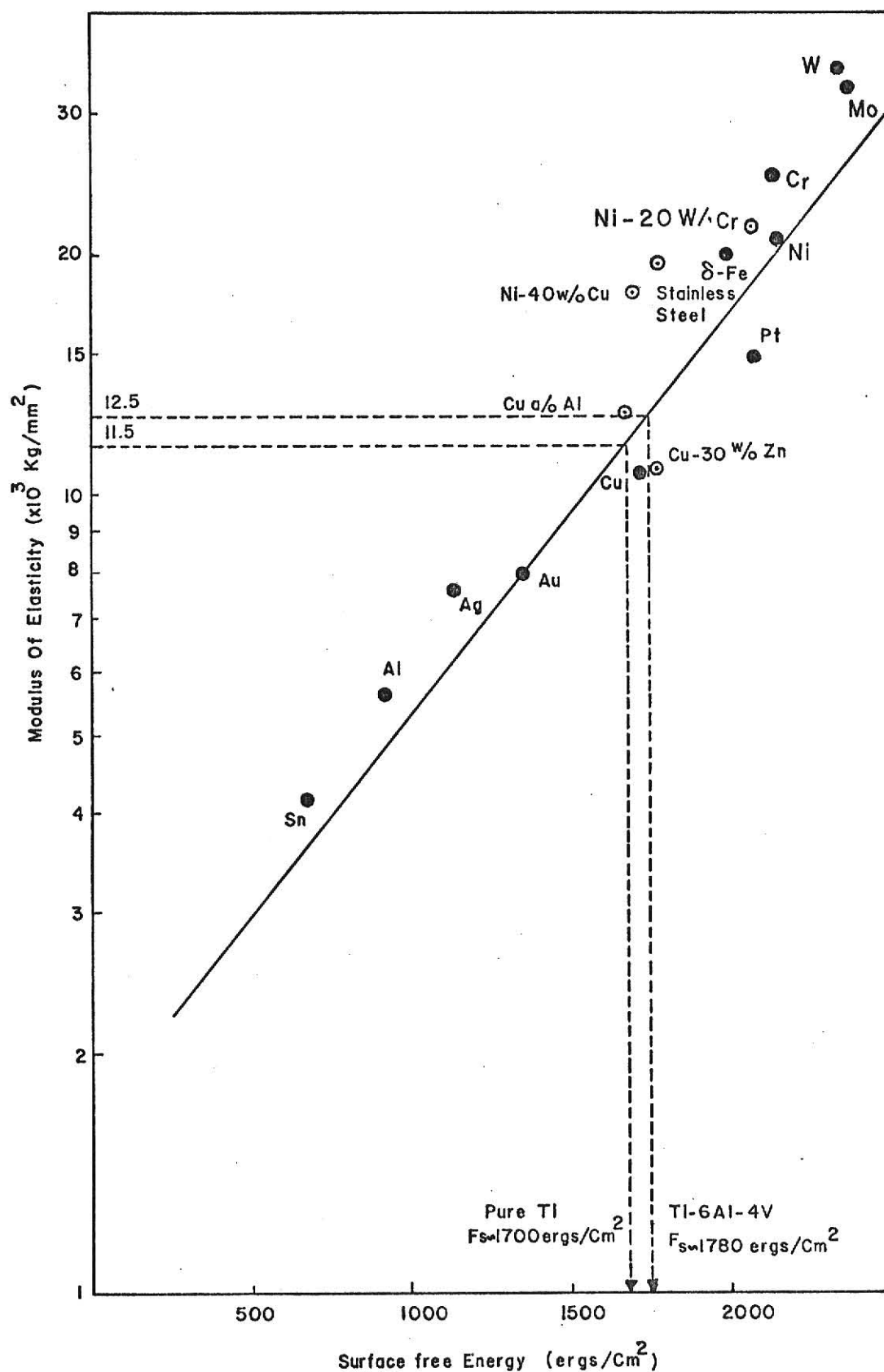


Fig. 23. Surface Free Energy of Solid Metals and Alloys Versus Modulus of Elasticity in Tension (Young's Modulus) at $0.9 T_m$ (Re-plotted from Murr, L.E., Interfacial Phenomena in Metals and Alloys, 1975).

its value is about $11.5 \times 10^3 \text{ kg/mm}^2$ (McQuillan and McQuillan, 1950) which is almost half that of iron, nickel, or cobalt (about $22 \times 10^3 \text{ kg/mm}^2$) although titanium has a higher melting point. The modulus of elasticity of pure titanium, as well as that for other pure metals, can be changed through the addition of alloying elements. Fedotov (1963) investigated the influence of the alloying elements on the elastic properties of pure titanium and found that small additions of aluminum (5 to 6% by weight) will greatly increase the elastic properties of pure titanium. These can be raised to twice that of the unalloyed titanium if the content of aluminum is further increased. Vanadium, however, has a relatively small effect in lowering the elastic properties of pure titanium. As a combined result of the addition of aluminum and vanadium to pure titanium, the Ti-6Al-4V alloy would therefore be expected to have a higher value of modulus of elasticity. Its value is approximately $12.5 \times 10^3 \text{ kg/mm}^2$ (Belfour, 1974). It is obvious from Fig. 23 that the surface free energy value of Ti-6Al-4V alloy should be higher than that of pure titanium. The straight line is obtained by least square calculation that employed only the pure metal values as indicated by the black data points of Fig. 23. The estimated values of surface free energy for pure titanium and the Ti-6Al-4V alloy obtained from this figure are 1700 and 1780 ergs/cm^2 , respectively. Using the temperature coefficient of the surface free energy from this study, extrapolated values of surface free energy at $0.9 T_m$ are 1800 ergs/cm^2 for pure titanium and 1900 ergs/cm^2 for the Ti-6Al-4V alloy. Comparison of the values obtained from Fig. 23 with the values found in this study shows reasonable agreement. The difference in the values found in this study and those values in Fig. 23 which is less

than 10% may arise from the uncertainty in the values of the modulus of elasticity for pure titanium and the Ti-6Al-4V alloy.

As is to be expected, the grain boundary free energies for the Ti-6Al-4V alloy found in this study are higher than those of pure titanium which is in agreement with the higher values of surface free energy found for the alloy as compared to those values found for the pure titanium. This of course is due in part to the interdependence of surface free energy and grain boundary free energy on each other. A slight reduction in the dihedral angles reported in Tables 7 and 12 due to the presence of the alloying elements is to be noted. The average angle for pure titanium is about 159° and that for the alloy is 156° . This suggests that the grain boundary free energy of the titanium has been increased to a greater degree due to the presence of the aluminum and vanadium. The ratios of the grain boundary to surface free energy given in Table 7 and 12 confirm this.

2) TEMPERATURE DEPENDENCE OF INTERFACIAL FREE ENERGIES IN PURE TITANIUM AND Ti-6Al-4V ALLOY

The experimentally determined temperature coefficients of the surface and grain boundary free energies for pure titanium and Ti-6Al-4V alloy are given in Table 14. The temperature coefficient of the interfacial free energy for solid metal and alloy is generally negative as necessitated by thermodynamics ideally described by

$$\left(\frac{d\gamma_I}{dT}\right)_V = -S_I - \sum_j \Gamma_j \frac{d\mu_j}{dT} \quad (7)$$

where γ_I is the interfacial free energy, S_I is the interfacial entropy, μ_j and Γ_j are the chemical potential and surface excess of the j th component.

Table 14. Temperature Coefficients of Surface and Grain Boundary Free Energies.

Material	dF_s/dT (ergs/cm ² °C)	$d\gamma_{gb}/dT$ (ergs/cm ² °C)
Pure titanium	-0.435	-0.65
Ti-6Al-4V alloy	-0.443	-0.10

For pure metals (a single-component system), if it is assumed that there is no nonequilibrium concentration of vacancies, then μ will be constant and Eq. (7) can be written as simply as

$$\left(\frac{d\gamma_I}{dT}\right)_v = -S_I \quad (8)$$

It is obvious, from Eq. (8), that the temperature coefficient of the surface free energy of an idealized (nonadsorbing) interface in a pure metal at elevated temperature will always be negative (entropy is always positive) and this value will tend to be positive for strong impurity adsorption at the interface.

Literature values of experimentally determined temperature coefficients of surface free energy for solid metals and alloys are extremely limited. Murr (1975) has summarized the known measurements of surface free energies associated with temperatures for solid metals and alloys. Most of them are obtained by the zero creep technique in inert gas atmosphere. He noted that the average value of the temperature coefficient of surface free energy for pure metals is found to be $-0.45 \text{ ergs/cm}^2\text{ }^\circ\text{C}$. Comparison of the temperature coefficients of surface free energy found in this study with the above average value shows good agreement of the temperature coefficient of surface free energy for both pure titanium ($dF_S/dT = -0.435 \text{ ergs/cm}^2\text{ }^\circ\text{C}$) and the Ti-6Al-4V alloy ($dF_S/dT = -0.443 \text{ ergs/cm}^2\text{ }^\circ\text{C}$).

The temperature coefficients of grain boundary free energies ($d\gamma_{gb}/dT$) have been measured for only a very small number of solid metals and alloys. The values obtained in this study fall in the range of those values, as summarized by Murr (1975), for other metals and alloys. Reported values of the grain boundary free energy temperature coefficients are in the

range -0.07 to -1.0 ergs/cm²°C. Comparison of the temperature coefficient of grain boundary free energies for pure γ -phase iron ($d\gamma_{gb}/dT = -1.0$ ergs/cm²°C) with 304 stainless steel, an Fe-Cr-Ni alloy, ($d\gamma_{gb}/dT = 0.49$ ergs/cm²°C) shows the same trend as that which was found in this study for pure titanium ($d\gamma_{gb}/dT = -0.65$ ergs/cm²°C) and the Ti-6Al-4V alloy ($d\gamma_{gb}/dT = -0.10$ ergs/cm²°C).

It can be noted, on comparing the temperature coefficients of grain boundary free energies with those of the surface free energy, that the value of $d\gamma_{gb}/dT$ for pure titanium is proportionately larger than the value of dF_s/dT while the value of $d\gamma_{gb}/dT$ for Ti-6Al-4V alloy is proportionately smaller than the value of dF_s/dT . The reason for these results is difficult to explain due to many factors involved such as the concentration and distribution of the alloying element in the titanium alloy, adsorption and segregation of solute and impurity atoms to solid surfaces and grain boundaries, etc. All these factors are beyond the scope of this present study.

3) SELF-DIFFUSION COEFFICIENT: NABARRO-HERRING MECHANISM

Nabarro (1948) proposed that creep can occur by diffusion exchange of vacancies between the grain boundaries and the free surface, so that a diffusion current is set up in each grain. Using this model for wires with a "bamboo" grain structure, Nabarro (1948) and Herring (1950) developed expressions for the creep rate which when applied to the creep of fine wires can be used to obtain an expression for the self-diffusion coefficient, D , in the form

$$D = \frac{2 \dot{\epsilon} \ell r R T}{\beta \Omega \sigma} \quad (9)$$

where $\dot{\epsilon}$ is the strain rate, $\bar{l}$ is the mean or average grain length, r is the wire radius, R is the gas constant, T is the absolute temperature, Ω is the molecular volume, σ is the resultant stress on the wire, and β is a parameter whose value depends on the ratio $\bar{l}/r$, and for $\bar{l}/r > 2$, $\beta \sim 12$.

Experimental results obtained in zero-creep studies provide enough data to calculate the value of self-diffusion coefficient from Eq. (8). The strain rate, defined as dc/dt , is obtained directly from the creep studies. The volume per gm. atom, Ω , of pure titanium is reported as $10.89 \times 10^{-3} \text{ m}^3/(\text{kg mole})$ at 900°C (Pearson, 1964). For Ti-6Al-4V alloy, the volume per gm. atom can be approximated by using average molecular weight analysis and the value obtained is $10.26 \times 10^{-3} \text{ m}^3/(\text{kg mole})$ at room temperature. Assuming that a 2.5% volume of the alloy increase at temperature near the melting point (Allen and Kingery, 1959), the value of volume per gm. atom for Ti-6Al-4V alloy used in Eq. (8) is $10.52 \times 10^{-3} \text{ m}^3/(\text{kg mole})$. Ω is taken as a constant through the calculations of the self-diffusion coefficient at various temperatures since the temperature difference between the various tests is small. The critical load, W_0 , divided by the cross-section area of the wire, $A = \pi r^2$, leads to the value of stress, σ , i.e., $\sigma = \frac{W_0}{\pi r^2}$. The calculated self-diffusion coefficients at four different temperatures for pure titanium and Ti-6Al-4V alloy are given in Tables 15 and 16 and comparison of the temperature dependence of the self-diffusion coefficient for both pure titanium and the Ti-6Al-4V alloy is shown in Fig. 24. The value of the self-diffusion coefficient for both pure titanium and the Ti-6Al-4V alloy increases as the temperature increases due to the higher thermal energies associated with these elevated temperatures. There is a

Table 15. Experimental Data and Results of Self-Diffusion Coefficients for Pure Titanium

Wire No.	Temperature, T		$\dot{\epsilon}$ ($\times 10^{-7}$ cm/cm-sec)	ℓ ($\times 10^{-2}$ cm)	σ ($\times 10^{-2}$ Kg/cm ²)	D ($\times 10^{-7}$ cm ² /sec)
	°F	°K				
Ti-88	2080	1410.8	0.233	1.372	26.133	0.142
Ti-81	2200	1477.4	0.903	1.358	25.730	0.580
Ti-54	2300	1533.0	1.556	1.340	26.409	0.997
Ti-17	2400	1588.6	2.137	1.422	25.628	1.550

Table 16. Experimental Data and Results of Self-Diffusion Coefficients for Ti-6Al-4V Alloy

Wire No.	Temperature, T		$\dot{\epsilon}$ ($\times 10^{-7}$ cm/cm-sec)	ρ ($\times 10^{-2}$ cm)	σ ($\times 10^{-2}$ Kg/cm ²)	D ($\times 10^{-7}$ cm ² /sec)
	°F	°K				
Ti-4V-51	2080	1410.8	1.591	1.393	27.719	0.962
Ti-4V-48	2150	1449.7	2.216	1.393	27.127	1.407
Ti-4V-22	2230	1494.1	1.569	1.400	26.338	1.063
Ti-4V-53	2345	1558.0	3.325	1.355	26.661	2.246

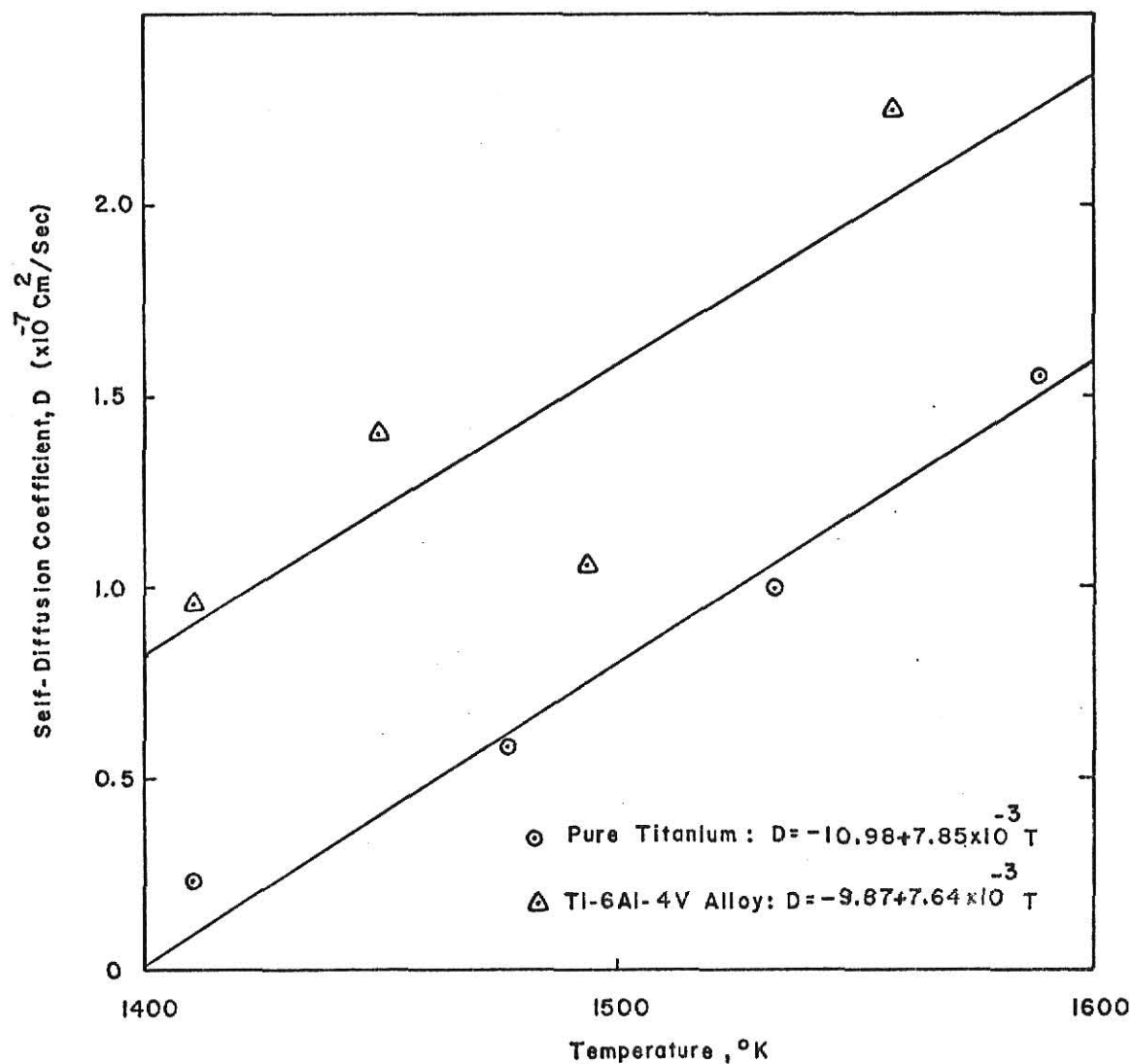


Fig. 24. The Dependence of Self-Diffusion Coefficients on Temperature for Pure Titanium and the Ti-6Al-4V Alloy.

greater probability for movement of vacancies as well as a greater equilibrium concentration of vacancies as the temperature increases. Since self-diffusion of the atoms is vacancy dependent, the increase in the self-diffusion coefficient with increasing temperature is as should be expected. Self-diffusion coefficient values of pure titanium found in this study are comparatively lower than those of the Ti-6Al-4V alloy but the temperature dependence of self-diffusion coefficients for both of these two materials are almost the same. Comparison of the results obtained in this study with those of the other metals and alloys reported in the literature shows the correct order of magnitude of self-diffusion coefficient for both pure titanium and the Ti-6Al-4V alloy.

4) ERROR IN MEASUREMENT OF SURFACE AND GRAIN BOUNDARY FREE ENERGIES OF PURE TITANIUM AND Ti-6Al-4V ALLOY.

The probable error of the computed values of the surface and grain boundary free energies for the materials under investigation is determined from the uncertainties in the terms of Eq. (5),

$$F_S = \frac{W_0}{\pi r [1 - 2r(n/l) \cos(\Omega_S/2)]} \quad .$$

Random errors such as measurement of the length of the wire specimens before and after creep anneals, weighing of the sample, small temperature variations, the number of grains per unit length counted through the microscope, etc., may vary from test to test. The length measurement of the wires before and after the creep tests is considered to be the most likely cause of random error due to the sensitivity of the strain on the obtained critical load. The measuring point on each gauge length of the wire before and after the creep test may not be the same and result in

the uncertain value in the strain. In this study, possible error in length measurements is found to be in the range of ± 0.0004 inch. Reduction of this error can be achieved by using x-ray techniques (Hondros, 1965) in which photographs, showing the measuring points in each gauge length, are taken before and after the creep anneal. In this way, a more accurate value of the strain is obtained.

There are two possible mechanisms which contribute to the deformation of the wires besides that of the Nabarro-Herring mechanism. The first one is kinking, which appears to be the result of rotation of the grain about an axis lying in the grain boundaries. Although some evidence of kinking of the wire specimens may be found in the more lightly stressed wires, the majority of the wire tested did not exhibit this phenomena which may occur in heating and cooling through the allotropic transformation temperatures of pure titanium and the Ti-6Al-4V alloy. Price (1963) found kinking to be dependent upon the stress and diameter of the wires. Kinking was found to occur less frequently in the most heavily stressed and thicker wires of his tests. Since the wires used in this present study were similar in size to the larger diameter wires used by Price and the stress levels were generally as large as or larger than his, the absence of kinking is entirely expected. The second deformation mechanism possible is offsetting which appears to be the result from the normal viscous behavior of grain boundaries. Since the offset movement is lateral to the direction of the applied stress and measured strain, the effect appears to be negligible and was not observed in the present work.

Surface contamination and surface-active impurities in the test materials also have a significant effect on the values of surface and

grain boundary free energies. In this study, precautions were taken to avoid the effect of surface contamination by using the high purity helium atmosphere since it cannot be physically adsorbed at these test temperatures. The appearance and ductility of the wires after the creep tests confirmed negligible surface contamination. Since high purity 99.97% titanium was used in this study, the effect of surface-active impurity can be neglected. For the Ti-6Al-4V alloy, the commercial grade was used for study and the content of carbon, oxygen, and nitrogen as given in Table 2 is comparatively higher than pure titanium. Since these three elements are used as part of increasing the tensile strength of the titanium alloy as illustrated in Fig.4, lower interfacial free energy values due to the surface-active impurities in the commercial Ti-6Al-4V grade than would be expected for a high purity Ti-6Al-4V are expected.

CHAPTER VI

CONCLUSIONS

Using the zero-creep of fine wire technique in a purified helium atmosphere and measurements of the dihedral angle at the base of thermally-etched grain boundary grooves, the surface and grain boundary free energies of pure titanium and the Ti-6Al-4V alloy have been investigated.

The following conclusions can be drawn from this work:

- 1) For pure titanium, the surface free energy, F_S , is found to be in the range of 1895-1980 ergs/cm², the grain boundary free energy, γ_{gb} , is in the range of 670-790 ergs/cm² and the ratio γ_{gb}/F_S is in the range of 0.34-0.40 over the temperature range 1138-1316°C (2080-2400°F). For the Ti-6Al-4V alloy, the surface free energy, F_S , is found to be in the range of 2010-2110 ergs/cm², the grain boundary free energy, γ_{gb} , is in the range of 810-915 ergs/cm² and the ratio γ_{gb}/F_S is in the range of 0.39-0.43 over the temperature range 1138-1285°C (2080-2345°F). Comparison of the results between these two materials shows that the interfacial free energies of pure titanium are approximately 100-150 ergs/cm² lower than those of the Ti-6Al-4V alloy.
- 2) The temperature coefficients of surface free energy and grain boundary free energy obtained for pure titanium are -0.435 ergs/cm²°C and -0.65 ergs/cm²°C, respectively. For the Ti-6Al-4V alloy, the temperature coefficient of surface free energy is -0.443 ergs/cm²°C and the temperature coefficient of grain boundary free energy is -0.10 ergs/cm²°C.

- 3) Self-diffusion coefficients, found by using the Nabarro-Herring mechanism, for pure titanium are comparatively smaller than those of the Ti-6Al-4V alloy. The values of the self-diffusion coefficient for these two materials are on an order of magnitude $10^{-7} \text{ cm}^2/\text{sec}$.

Comparison of the results found in this investigation with those reported values in the literature shows good agreement. This suggests that the experimentally determined interfacial free energies obtained for pure titanium and the Ti-6Al-4V alloy are reliable and true for the conditions of this study.

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Appendix

Wire composition of 99.97% pure titanium

Impurity Element	Content (ppm by weight)
C	78
H	4
O	63
N	6
Ag	<0.1
Al	15
As	1
Au	<0.02
Bi	<0.02
Ca	0.08
Cd	<0.4
Cl	0.1
Co	0.4
Cr	12
Cu	8
Fe	30
Ga	<0.1
Ge	<0.15
Hf	12
In	<0.05
Ir	<2
K	0.08
Li	<0.001
Mg	<15
Mn	1.2
Mo	<5
Na	<1
Nb	2
Ni	2
P	0.15
Pb	<0.03
Pd	<0.15
Pt	<0.04
Re	<0.08
Rh	<0.05
Ru	0.12
S	1.5
Sb	0.1
Si	3.5
Sn	3.5
Ta	<0.04
Ti	----
V	1
W	<0.04
Zn	<0.25
Zr	20
Rare Earths	<2

THE SURFACE AND GRAIN BOUNDARY FREE ENERGIES
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by

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ABSTRACT

The zero-creep of fine wires technique has been used to obtain the absolute values of surface and grain boundary free energies over a range of elevated temperatures in a purified helium atmosphere and under equilibrium conditions for pure titanium metal and the Ti-6Al-4V alloy, a principal metal and alloy used in the aerospace industry. The corresponding elevated temperature coefficients of the interfacial free energies and the ratio of grain boundary to surface free energy have also been determined. The creep of fine wires of the two materials whose grain boundaries form a "bamboo" structure under creep conditions is assumed to be linearly controlled by the Nabarro-Herring mechanism. The values of the self-diffusion coefficients of pure titanium and the Ti-6Al-4V alloy have been obtained and compared by using this model. The interfacial free energy and self-diffusion coefficient values for pure titanium are found to be smaller than those of the Ti-6Al-4V alloy. Comparison of the results of this study with values reported in the literature gives good agreement. It is believed that the results obtained in this work are the true values for the materials under the conditions of the investigation.