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INTERFACIAL ENERGIES OF SOME ELEMENTAL AND ALLOY AEROSPACE MATERIALS

FINAL REPORT

June 30, 1975 - December 31, 1977

Grant No. AFOSR-75-2868

Submitted By

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January 20, 1978

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This is the final report of a two-year research program on the interfacial (surface and grain boundary) free energies of some elemental and alloy aerospace materials funded by the Air Force Office of Scientific Research under Grant No. AFOSR-75-2868.

Previously unreported values of the grain boundary free energies for pure titanium and the titanium alloy Ti-6Al-4V and of the surface free energy for the titanium alloy, as well as a new value of the surface free energy for pure titanium, have been determined using the zero-creep technique for small

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INTERFACIAL ENERGIES OF SOME ELEMENTAL AND ALLOY AEROSPACE MATERIALS

ABSTRACT

This is the final report of a two-year research program on the interfacial (surface and grain boundary) free energies of some elemental and alloy aerospace materials funded by the Air Force Office of Scientific Research under Grant No. AFOSR-75-2868.

Previously unreported values of the grain boundary free energies for pure titanium and the titanium alloy Ti-6Al-4V and of the surface free energy for the titanium alloy, as well as a new value of the surface free energy for pure titanium, have been determined using the zero-creep technique for small diameter wires and measurements of the dihedral angle at the base of thermally-etched grain boundary grooves. The temperature coefficients of the surface free energies and of the grain boundary free energies, as well as the self-diffusion coefficients, for pure titanium and for the Ti-6Al-4V alloy are reported.

INTRODUCTION

The originally proposed research program planned to investigate the interfacial (surface and grain boundary) free energies of several pure metals and alloys of current technical importance as aerospace materials. The scope of the program was of necessity narrowed and limited to determining results for pure titanium and a widely used titanium-base alloy, Ti-6Al-4V. These results have been obtained and are presented in this final report.

The surface and grain boundary free energies of solid pure metals and alloys have a significant influence upon many properties and phenomena associated with the materials. The interfacial free energies are of particular importance in the understanding of adsorption and absorption, surface reactions and kinetics, nucleation and growth, friction and adhesion, melting and solidification, grain boundary migration and sliding, and certain aspects of the mechanical behavior of the materials. Of particular current interest and practical importance in the aerospace utilization of metals and alloys are fracture toughness and cyclic crack propagation properties, both of which are dependent upon the interfacial free energy. The toughness of a material breaking in a purely brittle fashion has been shown [1] to be determined by the surface free energy. When fracture is accompanied by plastic flow, as is the usual case for commercial metals and alloys, the stress developed at the tip of the crack in brittle fracture is controlled by the surface free energy. The surface free energy, F_s, must be at least equal to the stress required to break the atomic bonds, as given roughly [2] by

$$\sigma_i = (EF_s/a_o)^{1/2} \qquad (1)$$

where E is Young's modulus, a_o is the interplanar spacing of the cleavage planes, and σ_i is the ideal or theoretical strength. The surface free energy is therefore needed to estimate the ideal strength and thereby the stress at the crack tip. For the determination of critical crack size and rate of crack growth, the energy required for the formation of new surface is needed. Reliable values of the surface and grain boundary free energies should therefore be of current practical significance for the estimation of theoretical strengths and provide useful aircraft and missile materials design criteria.

Unlike most of the other physical properties of pure metals, reliable data for surface free energy values are not generally available. Even less data is available concerning grain boundary free energies. Interfacial free energy data for alloys is practically nonexistent. Due to the scarcity of suitable data, estimations of interfacial free energies of solids from more or less reliable rules, using other physical properties more easily obtained experimentally, is often necessary. For solid state considerations of interfacial free energy related problems, a typical practice is to take the known liquid metal surface tension values and to attempt to extrapolate back into the solid state, as suggested by Skapski [3]. The surface free energy at a temperature, T, below the melting point, T_m, can be approximated by

$$F_s \cong 1.2(\gamma_L)_m + 0.45(T_m - T) \tag{2}$$

where $(\gamma_L)_m$ is the liquid metal surface tension at the melting point. The above approximation of surface free energy is by Murr [4] and is based upon Skapski's original equation for calculating the value from knowledge of the atomic arrangement and heat of fusion. The surface free energy of the solid near its melting point may be from 10-33% greater than that of the liquid [5-8], i.e., a considerable difference may exist between the surface tension value of the liquid and the surface free energy value of the solid due to solidification. Since no experiments have been carried out to correlate the temperature coefficients found for liquid metals with those measured for the solid metal, the validity of extrapolated information is questionable. The need for experimentally determined surface and grain boundary free energy values is thus apparent.

The surface and grain boundary free energies may be reliably determined experimentally by simultaneously using zero-creep information and measurements of the dihedral angles at the intersections of the grain boundaries with the wire surface. In applying the zero-creep technique, gage marks are placed on fine wires and various amounts of additional weight are applied in tension to a series of the wires. The wires are given a short time anneal at or above the test temperature; they are cooled and straightened if necessary prior to measuring the distance between gage marks. At this point, the grain boundaries are usually revealed by thermal etching. The thermal etch 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 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. 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 [5, 9, 10] to be linearly controlled by a Nabarro-Herring mechanism. The tensile load for zero-creep, i.e., the balance load, is determined graphically by plotting the total strain versus the total stress. The number of grains in each gage 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 relationship between the surface energy, F_s, the grain boundary energy, γ_{gb}, the number of grains per unit length, n/ℓ, and the tensile load for zero-creep, W_o, has been shown [11] to be given by the expression

$$W_o = F_s \pi r - \gamma_{gb}(n/\ell)\pi r^2 = \pi r[F_s - \gamma_{gb} r(n/\ell)] \tag{3}$$

where r is the radius of the test wire.

When the grain boundaries of a polycrystalline metal are revealed as grooves during annealing at an elevated temperature, each groove develops in such a manner so that the resultant of two surface free energies and one grain boundary free energy vanishes along the line of the grain boundary intersection. Smith [12] has shown that after a sufficiently long anneal, the dihedral angle, Ω_s, at the base of the groove is 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 the surface free energy is independent of crystallogrphic orientation, the surface and grain boundary free energies resolve themselves according to the expression

$$\gamma_{gb} = 2F_s \cos(\Omega_s/2) \tag{4}$$

Because the wire surfaces consist of planes of many possible indices, the surface free energy measured by the zero-creep technique is an average value for the range of orientations in the surface of the wire. The value of the 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 taken as the median of the distribution of a large number of angle measurements.

Funk et al. [13] have stressed the importance of maintaining surface/vapor equilibrium in order to obtain the true surface free energy. Buttner [14] found this also to be the case for determining the true grain boundary free energy. By performing the experiments in an inert gaseous atmosphere, collision of the evaporating atoms of the test material with atoms of the inert gas ensure that enough of the metal atoms are reflected back to the metal surface to maintain equilibrium. This is opposed to the case of conducting the experiments in vacuum in which the pressure is maintained so low that evaporation of metal atoms is not counter-balanced and equilibrium is not attained.

Conducting the experiments in an atmosphere containing any of the more reactive gases, expecially those known to affect the surface and grain boundary free energies, as typically indicated by embrittlement of the metal, would provide values other than the true values obtained by this research. This may be shown by the following in which the gas is considered to be an impurity (component B) which reacts with the test metal. For a system containing the one gaseous impurity, a modified form of the Gibbs adsorption equation is used. The excess concentration of impurity, Γ_B, at an interface may be expressed as

$$\Gamma_B = - (1/RT)(\partial\gamma_I/\partial \ln X_B) \qquad (5)$$

where γ_I is the surface or grain boundary free energy, X_B is the interface mole fraction of B, R is the gas constant, and T is the absolute temperature.

If the interfacial free energy is lowered by the addition of B, the impurity is adsorbed on the surface when a gaseous impurity and can segregate to the surface and the grain boundaries if it is absorbed by the metal. If the interfacial free energy is raised by the addition of B, the impurity is rejected from the surface or grain boundaries. For most interfaces in solids, the $(\partial\gamma_I/\partial \ln X_B)$ term is negative because the contribution to the heat of solution of the impurity of the strain energy is reduced if the impurity migrates to the interface. The energy of the disorders at the interface is also reduced when such segregation or adsorption occurs.

Systematic investigations of the effects of the major gaseous impurities on the interfacial free energy values would be expected to provide useful information, particularly for the solution of numerous practical applications, e.g., surface and intergranular oxidation and embrittlement related to specific impurities. The object of the research however was to provide the more basic interfacial free energy values upon which furture studies of the effects of impurities, both those in the surrounding environment and those contained within the metal itself, may be based and used for comparison.

PROCEDURE

The results obtained in this research were determined by a two-step experimental procedure. First, the zero-creep technique, as developed by Udin et al. [15] and modified by Laidler [16], was applied to find the balance load which was determined by the change in the gauge length of fine 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, 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 recrystallized alumina 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 tube was closed at one end with the open end connected to the vacuum and helium atmosphere system. The experiments were performed in a 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 microsieve trap to remove any water vapor present. Evacuation of the system was accomplished by the use of a mechanical vacuum pump.

MARZ grade titanium, with a purity of 99.97% Ti, was used in the study. A standard grade commercial Ti-6Al-4V alloy, with a composition as given in Table 1, was selected for use in the study in order to provide interfacial free energy data with direct applications usefulness. Both test metals were obtained commercially in the form of wire drawn down to 0.0127 cm (0.005 in.).

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 made of pure titanium was tied to the bottom of the test wire. During the creep anneal, the weights on the wires tend to cause the wires to elongate, while the surface forces tend to cause the wires to shorten. The purpose of the zero-creep test is to determine the tensile load that just balances the opposing surface forces and therefore results in no

Table 1. Composition of the standard commercial grade Ti-6Al-4V alloy.

Elements	Percent	
	Min.	Max.
Aluminum	5.50	6.7500
Carbon	-	0.1000
Hydrogen	-	0.0125
Iron	-	0.3000
Nitrogen	-	0.0500
Oxygen	-	0.2000
Vanadium	3.50	4.5000
Other elements total	-	0.4000
Titanium	Balance	

elongation nor contraction of the wire. Estimates of the balance load for zero-creep, made from available data for the surface tension value for the liquid metal [17] were used to determine the amount of weight to be suspended from the wires. Knots were tied about 5 cm apart with several knots being tied in each wire to serve as gauge markers. The wires were 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 an initial anneal of about twenty hours at or near the test temperature in order to soften and straighten them prior to the initial measurement of the distance between gauge marks. The twenty-hour initial anneal was experimentally determined to be adequate to bring the metals into the steady-state creep range.

Prior to the initial anneal, the furnace chamber was flushed several times with dried high purity helium to insure that the wires would be exposed only to the desired atmosphere during the heat treatments. After the wires had cooled in the furnace, they were removed and the gauge lengths of the several (generally 7 or 8) specimens per wire were carefully measured. 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 initial anneal was adequate to allow the grains to grow to the apparent equilibrium size and shape and the wires, when examined under a microscope, displayed the desired 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 equal the diameter of the wire. After the initial anneals, as well as after the subsequent 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 ± 0.000127 cm (0.00005 in.). The grains were observed to have retained the bamboo structure developed during the initial 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. 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 as shown in Fig. 1. The balance load for zero-creep, W_o, was determined graphically from the least squares line of the plot of load versus strain.

The grain boundary groove angles 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. 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.

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. (4) for γ_{gb} into Eq. (3) results in a single expression for the average surface free energy,

$$F_s = W_o/\{\pi r[1 - 2(n/\ell)r \cos(\Omega_s/2)]\} \qquad (6)$$

Substitution of the experimental parameters into Eqs. (6) and (4) gave the absolute values of the surface and grain boundary free energies of the wire specimens for each creep test.

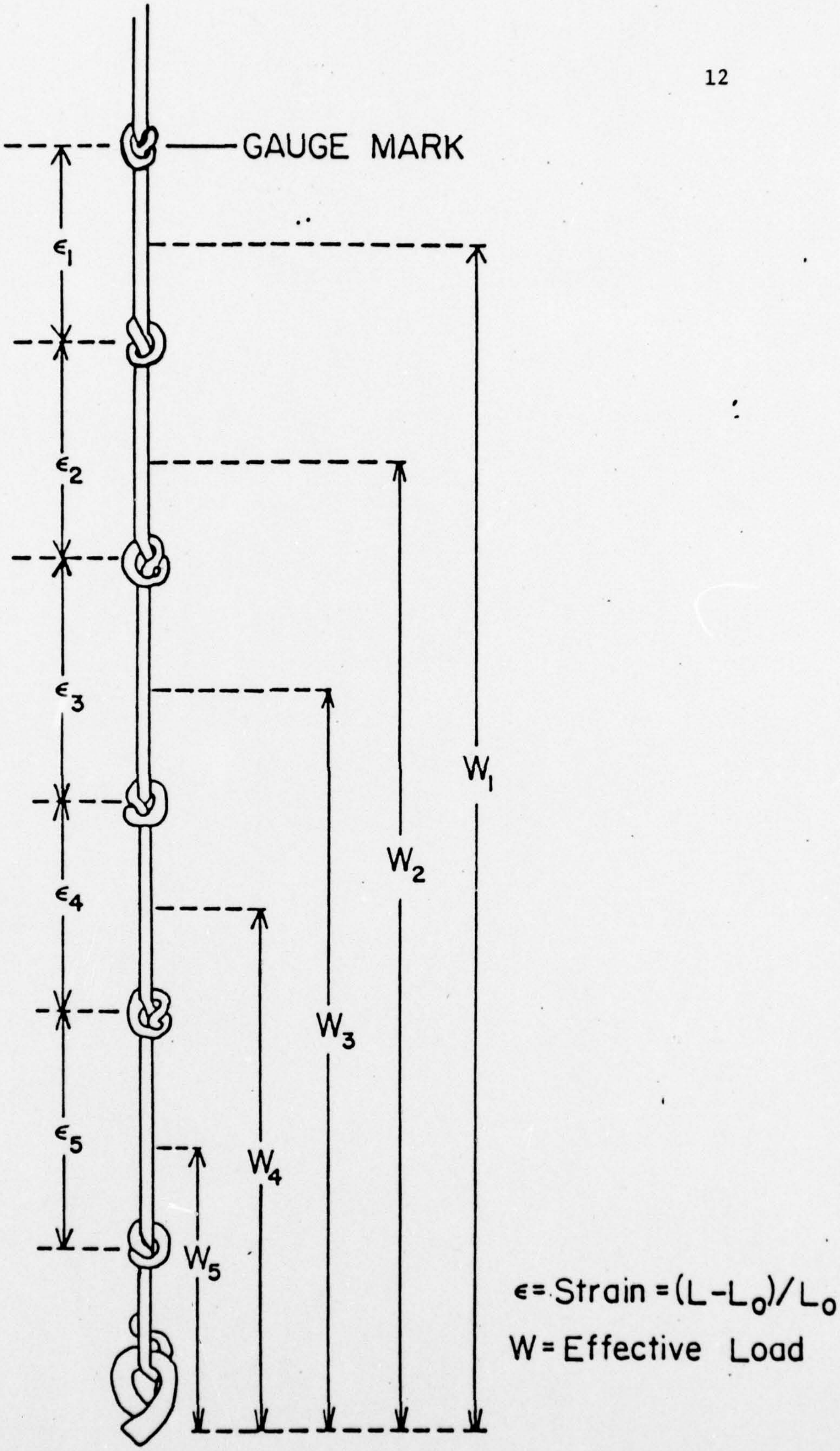

Fig. 1. Typical wire specimen showing how the effective loads, W, and strains, ϵ, were determined.

RESULTS

The experimental determination of the surface and grain boundary free energies of pure titanium and the Ti-6Al-4V alloy in a purified helium atmosphere were conducted at four different temperatures for each material. For pure titanium, the tests were performed at 1137.8°C (2080°F), 1204°C (2200°F), 1260°C (2300°F), and 1315.6°C (2400°F). The test temperatures for the Ti-6Al-4V alloy were 1137.8°C (2080°F), 1176.7°C (2150°F), 1221.1°C (2230°F), and 1285°C (2345°F). The experimental data and results for pure titanium are summarized in Table 2. The experimental data and results for the Ti-6Al-4V alloy are summarized in Table 3.

Several wires with several gauge lengths (6 to 9) were used to investigate the interfacial free energies at each test temperature. The interfacial free energies at each temperature reported in Tables 2 and 3 are considered to be the best values of the several tests which showed good reproducibility. Using the vertical travelling micrometer microscope, gauge length measurements were made on each section of wire specimens before and after the creep anneals. The resulting strains, reported as change in length per unit original length were plotted on linear coordinates versus the corresponding applied loads. A least square calculation was used to determine the most probable critical load at zero strain. A typical plot of these data for pure titanium at 1315.6°C (2400°F) is shown in Fig. 2. The critical load obtained for pure titanium on each test is in the the range of 32.5-33.5 mg. For the 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 anneal since the grains have recrystallized and grown to an equilibrium size and shape during this anneal. The average

Table 2. Summary of the Experimental Data and Results of Surface and Grain Boundary Free Energy for Pure Titanium.

Temperature		Creep time (hrs.)	Average n/ℓ	Average angle, Ω_s	Critical load, W_o (mg)	Surface free energy, F_s (ergs/cm^2)[a]	Grain boundary free energy, γ_{gb}, (ergs/cm^2)[a]	γ_{gb}/F_s
°C	°F							
1137.8	2080	96	185.07	157.83	33.11	1980	760	0.38
1204.4	2200	96	187.04	156.95	32.60	1970	785	0.40
1260.0	2300	98 3/4	189.54	160.26	33.46	1965	675	0.34
1315.6	2400	23 1/2	178.63	159.66	32.47	1895	670	0.35

[a] Values of surface free energy and grain boundary free energy are given in units of ergs/cm^2. This unit is identical to the SI (Système International) unit, millijoules per square meter (mJ/m^2).

Table 3. Summary of the Experimental Data and Results of Surface and Grain Boundary Free Energy for the Ti-6Al-4V alloy.

Temperature		Creep time (hrs.)	Average n/ℓ	Average angle, Ω_s	Critical load, W_o (mg)	Surface free energy, F_s (ergs/cm^2)	Grain boundary free energy, γ_{gb}, (ergs/cm^2)	γ_{gb}/F_s
°C	°F							
1137.3	2080	60	182.27	157.71	35.12	2095	810	0.39
1176.7	2150	96	182.28	154.89	34.37	2110	815	0.39
1221.1	2230	115	181.41	156.60	33.37	2010	815	0.40
1285.0	2345	60	187.47	156.59	33.78	2050	830	0.40

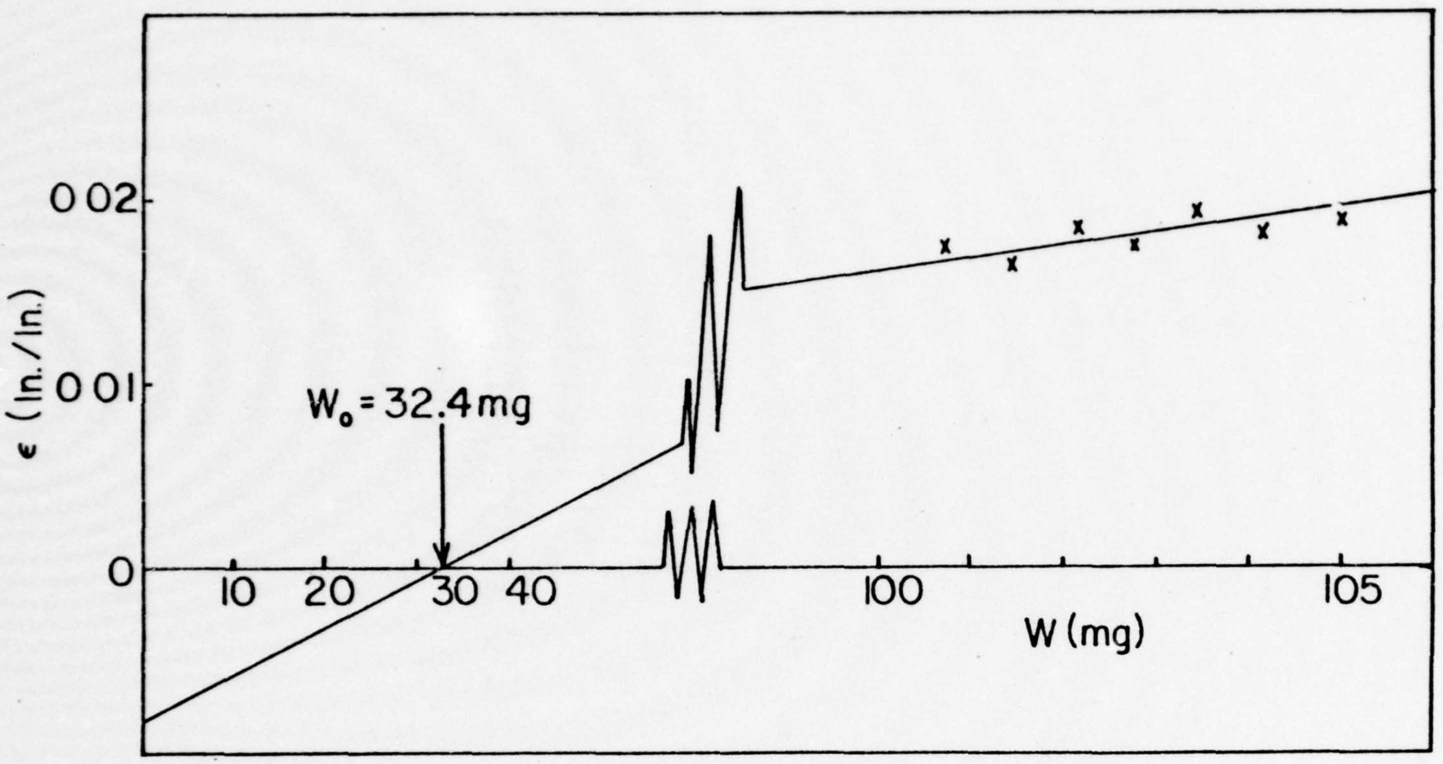

Fig. 2. Typical experimental load-strain plot for pure titanium at 1315.6°C (2400°F).

value for the number of grains per inch on each test of pure titanium is in the range of 179-190 and for the 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 thermally-etched groove at the intersection of the grain boundary with the surface of the wire which was formed during the 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 were evident. Direct angle measurements were made from enlarged photographic prints and the average dihedral angle was determined from many separate angle measurements made on the wire specimens of 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.

Using the value of surface free energy computed from Eq. (6) the corresponding grain boundary free energy was determined from Eq. (4). The ratio of grain boundary to surface free energy was also 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 equations. The error in the computed values was found to be generally in the range of ± 5 to 10% (standard deviation).

The variation of surface free energy and grain boundary free energy with temperature for pure titanium is illustrated in Fig. 3 and that for the Ti-6Al-4V alloy is shown in Fig. 4. 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

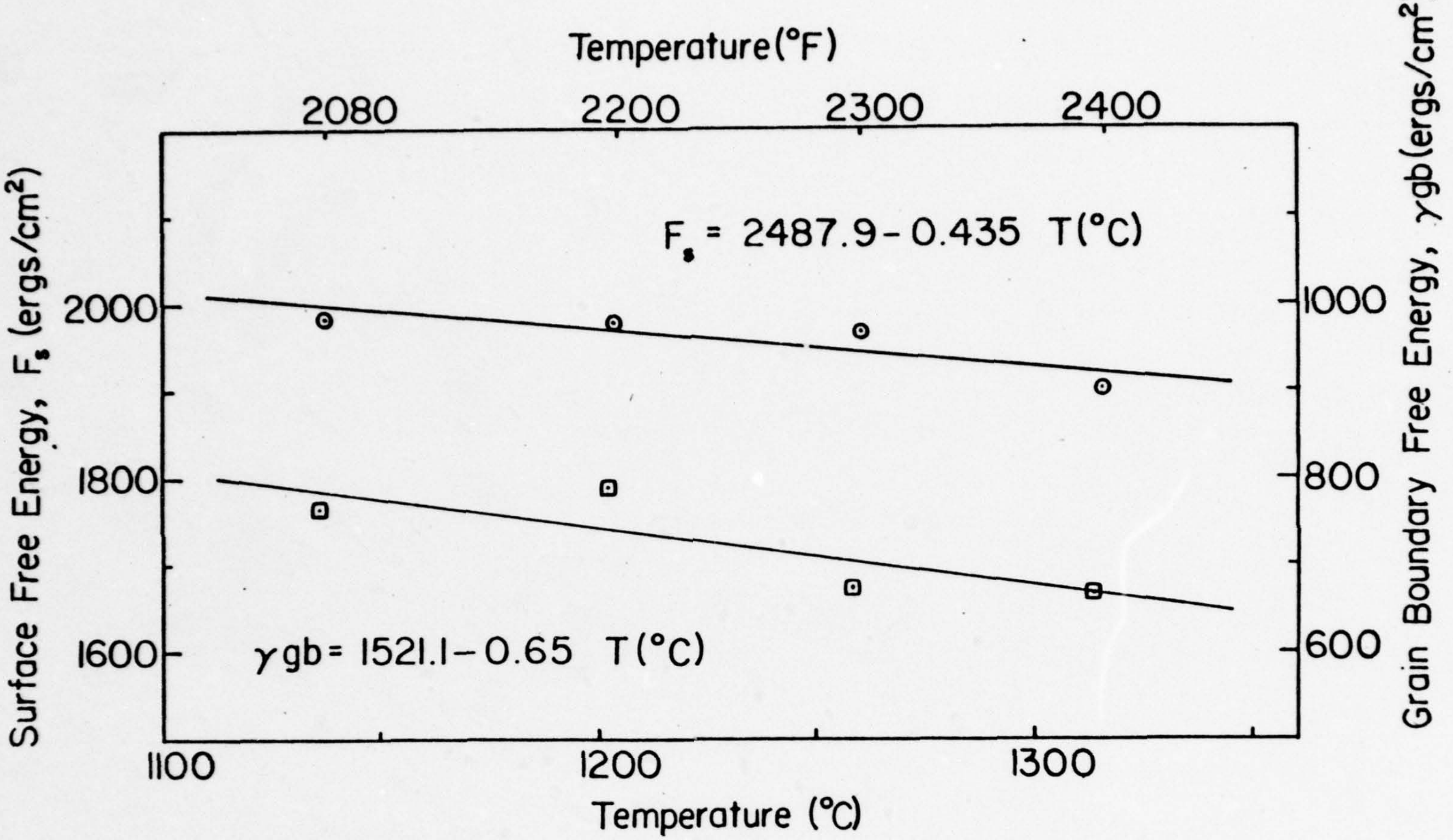

Fig. 3. The temperature dependence of the surface free energy (circles) and the grain boundary energy (squares) of pure titanium.

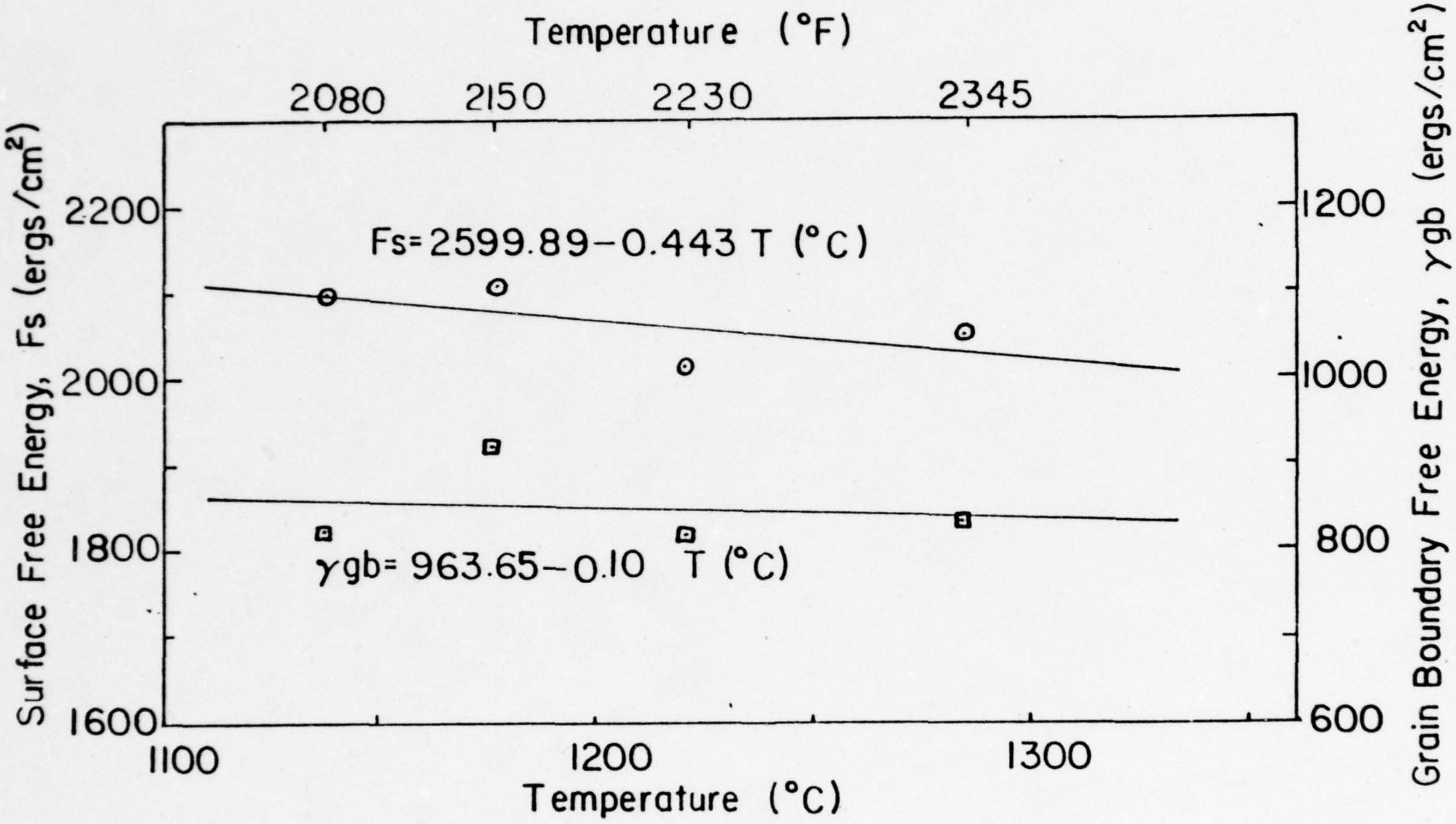

Fig. 4. The temperature dependence of the surface free energy (circles) and the grain boundary free energy (squares) of the Ti-6Al-4V alloy.

energy is -0.435 ergs/cm^{2o}C and the temperature coefficient of grain boundary free energy is -0.65 ergs/cm^{2o}C. For the Ti-6Al-4V alloy, the temperature coefficient of surface free energy and grain boundary free energy is -0.443 ergs/cm^{2}°C and -0.10 ergs/cm^{2o}C, respectively.

DISCUSSION

Due to the scarcity of published data on the solid state interfacial free energies of the two metals of this study, very limited comparison with such values is possible to confirm the validity of these results. Only one prior investigation has considered the surface free energy of titanium; results concerning the grain boundary free energy of titanium have not been reported; and, no data on either the surface or the grain boundary free energies of the Ti-6Al-4V alloy are to be found in the literature. Since accepted values of the surface tension of liquid titanium are more readily available, the initial verification of these results has been made by extrapolating and comparing the value of the surface free energy of titanium found in this study with an earlier published value of the surface tension of liquid titanium at the melting point. Using the temperature coefficient of the surface free energy for titanium of this study, extrapolation to the melting point (1730 ^{o}C) results in a value of surface free energy of about 1735 ergs/cm^{2}. Evidence suggests that a solid near its melting point may have a surface free energy value 10 to 33% higher than the liquid [5-8, 18, 19]. Assuming that the surface free energy of solid titanium is 10% higher than that of liquid titanium at its melting point, the estimated value of surface tension for liquid titanium for this work is found to 1560 ergs/cm^{2}. The best value of surface tension for liquid titanium at its melting point is reported by Allen [17] as 1650 ± 50 ergs/cm^{2}. 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 (less than 10%) between the value found in this study and that of Allen may be the result of the difference in the compositions of the titanium used in the two studies.

Using the surface free energy value for titanium at the melting point obtained by the extrapolation of the data of this study, $F_{s(mp)} = 1735$ ergs/cm^2, and Allen's value of the surface tension for liquid titanium at the melting point, $\gamma_{l(mp)} = 1650$ dynes/cm, the increase in energy due to solidification may be expressed as $F_{s(mp)} = 1.05\gamma_{l(mp)}$.

Kostikov et al. [20] reported the value of the surface free energy for titanium as approximately 1700 ergs/cm^2 at 1600°C. By extrapolating the value found in this work to 1600°C, a value of 1790 ergs/cm^2 is obtained. Attempts at comparison of this value with that of Kostikov et al. in order to explain this slight difference are considerably restricted due to the brevity of their report. Kostikov et al. did report $F_{s(mp)} = 1.22\gamma_{l(mp)}$ which is 17% greater than the value found in this study, 7% greater than the value attributed to Zadumkin and Karashayev [21], and 15% greater than the value attributed to Shcherbakov [22]. The relationship between $F_{s(mp)}$ and $\gamma_{l(mp)}$ found in this study is in good agreement with Shcherbakov's $F_{s(mp)} = 1.07\gamma_{l(mp)}$.

Murr [4] in his review of interfacial phenomena, has shown from the work of numerous previous studies that γ_{gb}/F_s ranges from 0.24 to 0.45. Lacking specific information on either F_s or γ_{gb}, the usual practice is to assume that the grain boundary free energy is about one-third of the surface free energy. The grain boundary free energy values for titanium obtained in this study are in the range of 670-790 ergs/cm^2 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 indicates a reasonable order of magnitude for the grain boundary free energies obtained. The values of γ_{gb}/F_s also give good agreement with reported studies for other pure metals.

Comparison of the interfacial free energies of the two metals of this study, using Figs. 3 and 4, indicates that 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 $ergs/cm^2$. Murr [4] has plotted the value of surface free energy of solid metals and alloys versus the modulus of elasticity at 0.9 T_m (the melting point) as shown in Fig. 5. 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 has a relatively low elastic constant and its value is about 11.5×10^3 kg/mm^2 [23]. 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 [24] 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 if further increased. Vanadium was found to have 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 may therefore be expected to have a higher value of modulus of elasticity. Its value is reported [25] as approximately 12.5×10^3 kg/mm^2. It is apparent then from Fig. 5 that the surface free energy value of the Ti-6Al-4V alloy would be higher than that of pure titanium.

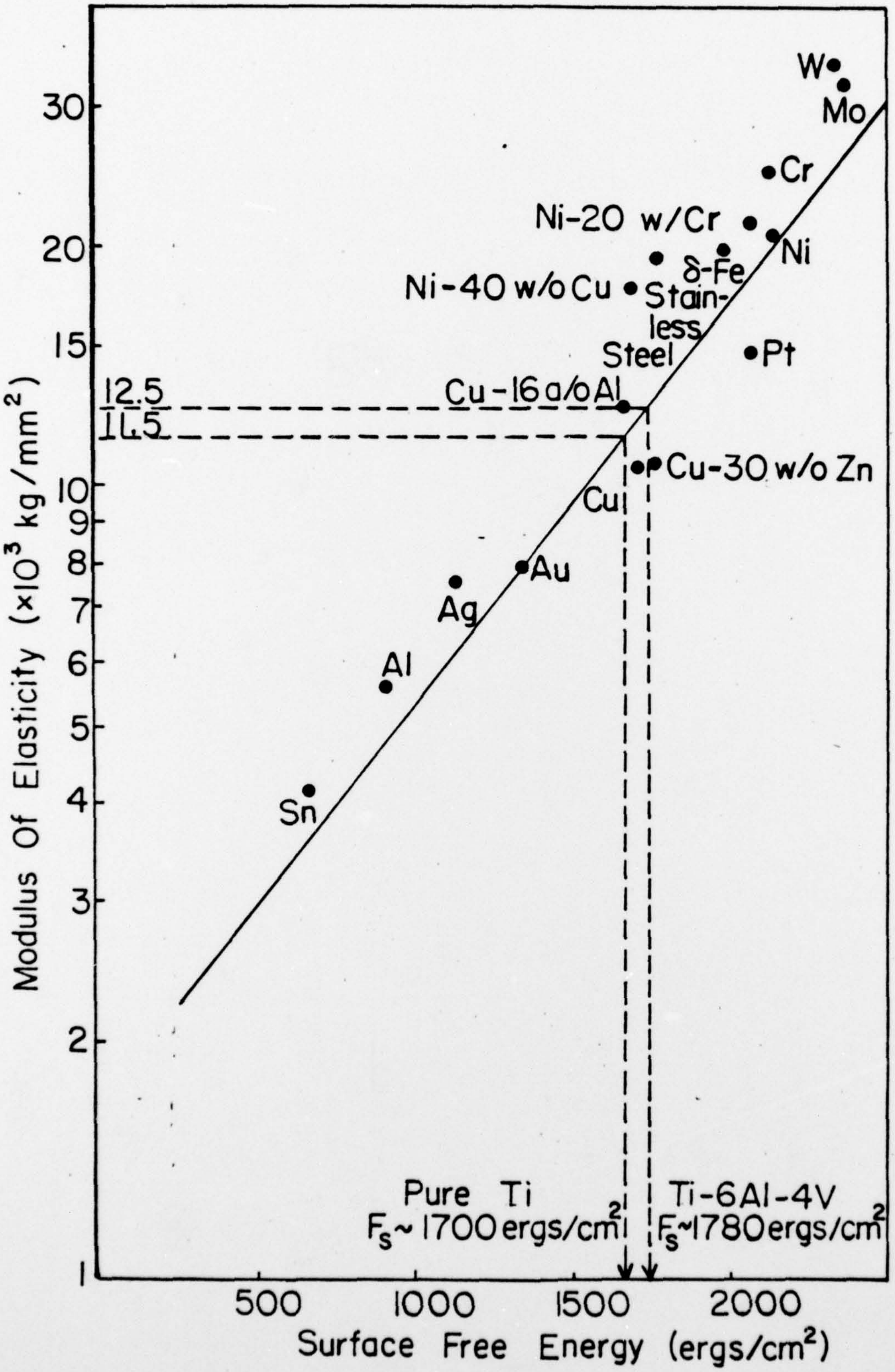

Fig. 5. Surface free energy of solid metals and alloys versus modulus of elasticity in tension (Young's modulus) at 0.9 T_m (°C). (After Murr [4]).

The estimated values of surface free energy for pure titanium and the Ti-6Al-4V alloy obtained from Fig. 5 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. The difference in the values found in this study and those values in Fig. 5 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 well as from the obvious fact that the data points of Fig. 5 do not all fall exactly on the least squares line. The significance of the comparison projected onto Fig. 5 lies in the realization that the surface free energy of the Ti-6Al-4V alloy may be greater than that of pure titanium. The difference in the surface free energy values of the two metals found from this rather approximate comparison on Fig. 5 (about 80 ergs/cm^2) when compared with the difference obtained experimentally (about 100 ergs/cm^2) are in reasonable agreement.

As may 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 2 and 3 due to the presence of the alloying elements is to be noted. The average angle for pure titanium is about 159^o and that for the alloy is 156^o. This suggests that the grain boundary free energy of the titanium alloy has been increased to a greater degree than that of the unalloyed titanium due to the presence of the aluminum and vanadium. The ratios of the grain boundary to surface free energy given in Table 2 and 3 confirm this.

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

$$(d\gamma_I/dT)_v = -S_I - \sum_j \Gamma_j \, (d\mu_j/dT) \tag{7}$$

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 jth component.

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 simply as

$$(d\gamma_I/dT)_v = -S_I \tag{8}$$

It is apparent, 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 [4] 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 atmospheres. The average value of the temperature coefficient of surface free energy for

Table 4. Temperature coefficients of the 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

pure metals is found to be -0.45 ergs/cm^2°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 ergs/cm^2°C) and the Ti-6Al-4V alloy (dF_s/dT = -0.443 ergs/cm^2°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, 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/cm^2°C. Comparison of the temperature coefficient of grain boundary free energies for pure γ-iron ($d\gamma_{gb}/dT$ = -1.0 ergs/cm^2°C) with 304 stainless steel, an Fe-Cr-Ni alloy, ($d\gamma_{gb}/dT$ = -0.49 ergs/cm^2°C) shows the same trend as that which was found in this study for pure titanium ($d\gamma_{gb}/dT$ = -0.65 ergs/cm^2°C) and the Ti-6Al-4V alloy ($d\gamma_{gb}/dT$ = -0.10 ergs/cm^2°C).

Nabarro [26] proposed that creep can occur by the 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 [26] and Herring [27] 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

$$D = (2\dot{\varepsilon}\ell rRT)/(\beta\Omega\sigma) \quad (9)$$

where $\dot{\varepsilon}$ is the strain rate, ℓ is the mean 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 ℓ/r, and for $\ell/r>2$, $\beta \sim 12$.

Experimental results obtained in zero-creep studies provide enough data to calculate the value of self-diffusion coefficient from Eq. (9). The strain rate, $d\varepsilon/dt$, is obtained directly from the creep studies. The volume per gram-atom, Ω, of pure titanium is reported as 10.89×10^{-3} $m^3/(kg\ mole)$ at 900°C [28]. For the Ti-6Al-4V alloy, the volume per gram-atom can be approximated by using average molecular weight analysis and the value obtained is $10.26 \times 10^{-3} m^3/(kg\ mole)$ at room temperature. Assuming a 2.5% volume increase for the alloy at temperatures near the melting point [29], the value of volume per gram-atom for Ti-6Al-4V alloy used in Eq. (9) is $10.52 \times 10^{-3} m^3/(kg\ mole)$. 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_o, divided by the cross-sectional area of the wire, $A = \pi r^2$, leads to the value of stress, σ, i.e., $\sigma = W_o/\pi r^2$. The calculated self-diffusion coefficients at four different temperatures for pure titanium and the Ti-6Al-4V alloy are given in Table 5.

Table 5. Experimental data and results for the self-diffusion coefficients for pure titanium and the Ti-6Al-4V alloy.

Temperature, T		$\dot{\varepsilon}$	ℓ	σ	D
°K	°F	($\times 10^{-7}$ cm/cm-sec)	($\times 10^{-2}$ cm)	($\times 10^{-2}$ kg/cm^2)	($\times 10^{-7}$ cm^2/sec)
			Titanium		
1410.8	2080	0.233	1.372	26.133	0.142
1477.4	2200	0.903	1.358	25.730	0.580
1533.0	2300	1.556	1.340	26.409	0.997
1588.6	2400	2.137	1.422	25.628	1.550
			Ti-6Al-4V		
1410.8	2080	1.591	1.393	27.719	0.962
1449.7	2150	2.216	1.393	27.127	1.407
1494.1	2230	1.569	1.400	26.338	1.063
1558.0	2345	3.325	1.355	26.661	2.246

Comparison of the temperature dependence of the self-diffusion coefficient for both pure titanium and the Ti-6Al-4V alloy is shown in Fig. 6. 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 greater probability for movement of vacancies as well as a greater equilibrium concentration of vacancies as the temperature increases. The self-diffusion coefficient values for pure titanium found in this study are comparatively lower than those for the Ti-6Al-4V alloy but the temperature dependence of the self-diffusion coefficient for both of these two materials is 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.

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.

For pure titanium, the surface free energy is found to be in the range of 1895-1980 ergs/cm^2 and the grain boundary free energy is in the range of 670-790 ergs/cm^2 over the the temperature range 1138-1316°C (2080-2400°F). For the Ti-6Al-4V alloy, the surface free energy is found to be in the range of 2010-2110 ergs/cm^2 and the grain boundary free energy is in the range of 810-830 ergs/cm^2 over the temperature range 1138-1285°C (2080-2345°F).

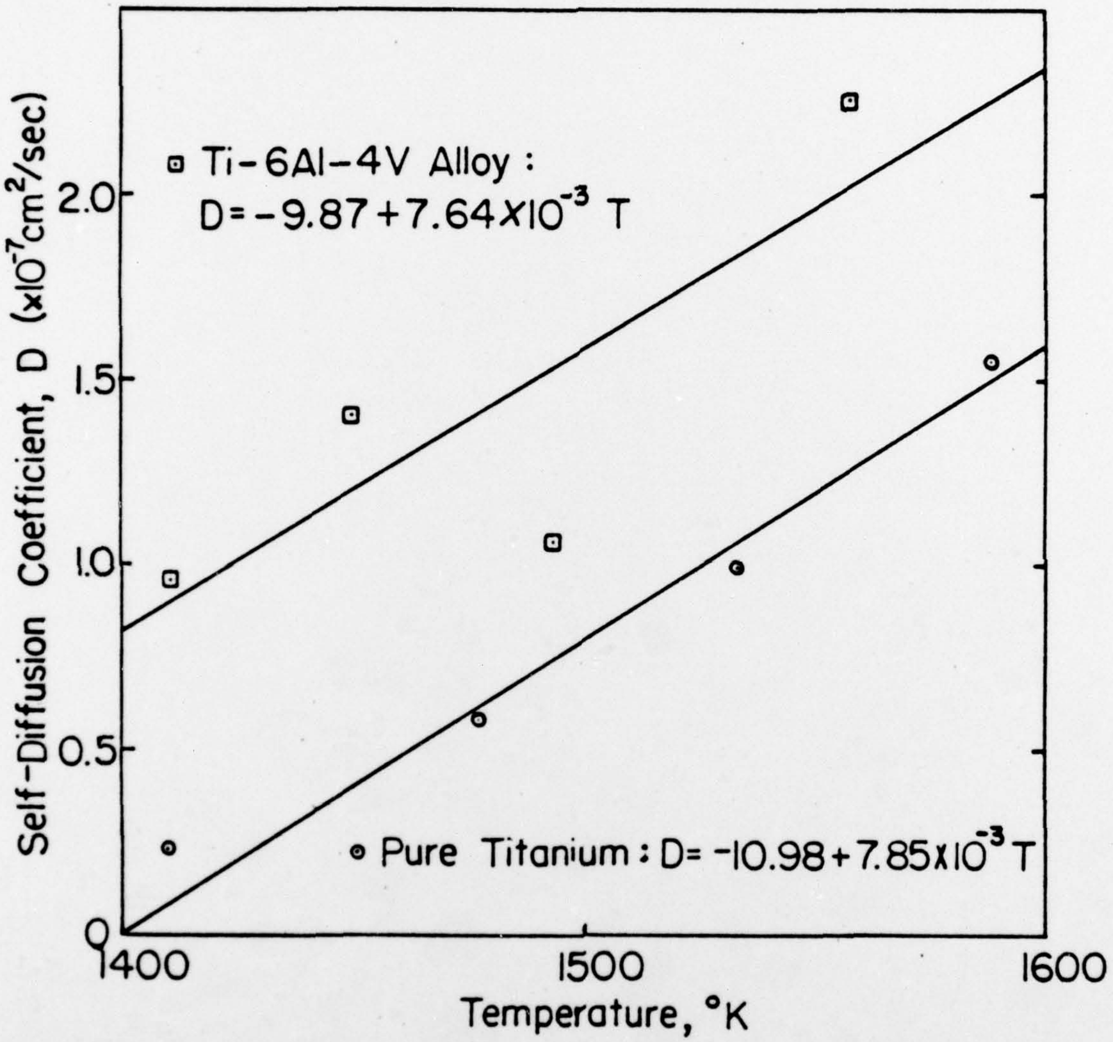

Fig. 6. The dependence of the self-diffusion coefficients on temperature for pure titanium and the Ti-6Al-4V alloy.

The temperature coefficients of surface free energy and grain boundary free energy obtained for pure titanium are -0.435 ergs/cm^2°C and -0.65 ergs/cm^2°C, respectively. For the Ti-6Al-4V alloy, the temperature coefficient of surface free energy is -0.443 ergs/cm^2°C and the temperature coefficient of grain boundary free energy is -0.10 ergs/cm^2°C.

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} cm^2/sec.

OTHER ACCOMPLISHMENTS OF THE RESEARCH PROGRAM

In addition to the investigation to determine the above interfacial free energy information, the results of the research have been the basis for the master's thesis [30] of the one graduate student in chemical engineering who assisted in the program and are the basis of a paper recently submitted for publication in Materials Science and Engineering entitled "The Surface and Grain Boundary Free Energies of Pure Titanium and the Titanium Alloy Ti-6Al-4V." As described in the first Annual Report (July 30, 1976) of this research program, a major accomplishment expected to result from this program is the development of a materials science program at Kansas State University.

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