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COMPARISON OF THE TEMPERATURE-DEPENDENT ELASTIC MODULUS OF TI-F--ETC(U)

OCT 80 J R NEIGHBOURS, A C EHRlich

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**Comparison of the Temperature-Dependent
Elastic Modulus of Ti-Fe
with H-Doped Ti-Fe in the [111] Direction**

J. R. NEIGHBOURS

*U.S. Naval Postgraduate School
Monterey, CA 93940*

and

A. C. EHRLICH, R. A. MASAMURA, AND C. L. VOLD

Material Science and Technology Division

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COMPARISON OF THE TEMPERATURE-DEPENDENT ELASTIC MODULUS OF Ti-Fe WITH H-DOPED Ti-Fe IN THE [111] DIRECTION

INTRODUCTION

In recent years a large amount of new research activity has been undertaken in the area of hydrogen in metals. This interest arose primarily for two diverse reasons; (a) hydrogen alloys of palladium were found to be superconducting though palladium is not; (b) hydrogen is a potential portable fuel, and metal hydrides are a promising means of storing hydrogen safely and conveniently. Currently, the leading material for use in hydrogen storage is the intermetallic compound TiFe. Although considerable effort has been devoted to studying the electronic, physical, and metallurgical properties of TiFe, much is not yet understood. This is true for dilute hydrogen alloys as well as for the more concentrated materials.

In the dilute hydrogen regime absorption and desorption data have been obtained wherein the hydrogen content as a function of hydrogen pressure is measured. When these data are plotted as the square root of hydrogen pressure *vs* hydrogen concentration, deviations from linearity are obtained for hydrogen to metal concentrations above approximately 5% and below approximately 1%. Whereas the deviation at 5% hydrogen is known to be associated with a cubic to orthorhombic phase transition, the behavior at 1% is still unexplained. Thus it is of interest to investigate other fundamental properties of dilute alloys of hydrogen in TiFe. In this study, we report measurements of the change in the velocity of sound as a function of temperature when hydrogen is added to a single crystal of TiFe.

EXPERIMENTAL

The TiFe specimen used in these experiments was sectioned from a single crystal obtained from Dr. George Kamm of the Naval Research Laboratory, who grew it using an electron beam zone melting apparatus. The original crystal was a nearly circular cylinder rod of approximately 1/8 in. diameter and 4 in. length. The specimen used in this work was cut from the rod using a standard spark cutting rig. After cutting, the ends were first spark planed and then hand lapped so that the resulting faces were flat and perpendicular to the cylinder axis. The finished specimen has a measured length of 0.4525 ± 0.0001 in.

Etching¹ showed the specimen to be composed principally of a single crystal with a small needle-like grain running down one side. A back reflection Laue picture showed the orientation of the cylinder axis of the rod (main crystal) to be within 1.5° of [111]. Before and after etching, the appearance of the specimen was silver metallic.

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¹Bath composed of 7 cm³ HCl, 2 cm³ HF, and water to make 50 cm³.

The sample chamber was a demountable heavy-walled copper cylinder with a standard BNC fitting at one end. An interior spring-loaded electrode assured contact with the transducer. Temperature was measured using a chromel *vs* gold-0.07 at. % iron thermocouple, one junction of which was fastened into a small hole in the base of the sample chamber. Thermal contact was enhanced by filling the void between the thermocouple and the sides of the hole with a high-conductivity grease. The thermal emf was measured against a standard ice bath using a high-impedance digital voltmeter.

Temperature was determined from a standard temperature scale which had been slightly corrected for low-temperature deviations. The error in temperature using this method is estimated to be less than 0.5°K at temperatures below 77°K and less at higher temperatures. Several electrical resistance heaters were also attached to the copper sample chamber. These were not used for temperature control but only for warming the chamber and sample. Thermal inertia was great enough so that the temperature was essentially constant over the time period necessary for an ultrasonic measurement.

Small signals from the 1/8-in. diameter quartz transducers along with other noise and triggering problems precluded operation of the ultrasonic apparatus in its original sing-around mode. Instead, the apparatus was reconstituted as a conventional [1,2] single transducer pulse echo apparatus using an Arnborg pulser and amplifier. The best configuration used two double stub tuners with the 1/8-in. diameter 20 MHz quartz transducer driven at the third harmonic. Higher harmonics were not possible because of the rapid dropoff of the amplifier.

Transit time measurements of two types were performed. Some were carried out by measuring the time of occurrence of each detectable echo and fitting the graph of the time *vs* echo number with a straight line. These "absolute measurements" required a period of time and were carried out at constant temperature. Some of these results are shown in Table 1. Other, relative measurements were carried out by setting a fiducial mark on a particular echo and observing the change in position of the echo on the calibrated oscilloscope screen as the temperature changed.

After the ultrasonic measurements of pure TiFe were completed, hydrogen was diffused into the lattice. This was done by heating the sample at moderately elevated temperature in a hydrogen atmosphere and then quenching the sample in water at the end of the heat treatment. The first attempt was heating for 1 hour @ 750°C at a hydrogen gauge pressure of 1 atm. This treatment had no effect on the appearance of the sample or the velocity of sound.

A second heat treatment at the same hydrogen pressure was more complex. One half hour at 700°C was followed by a quick reduction in temperature to 600°C where the sample remained for 2 hours. The temperature of the sample was then quickly reduced to 500°C and held there for 20 hours. At the end of this period, the system was flushed with helium and the sample was quickly removed and quenched.

After this lengthy heat treatment, the sample appearance was black with some minor cracking along the sides. A change in dimension was also observed; the new measured length was 0.4515 in. However, it was still possible to propagate 60 MHz waves so another set of absolute and differential measurements was performed. No effect on attenuation was observed as a result of the heat treatment.

Table 1—Room-Temperature Lengths and Observed Transit Times for 60 MHz Longitudinal Waves

Specimen	Length (cm) 296° K	Time Between Pulses (μsec)		
		296° K	77° K	4.2° K
TiFe	1.1494	3.626	3.581	3.579
TiFe ± H	1.1468	3.613	3.625	3.575

After the ultrasonic measurements on this hydrogen treated TiFe compound, the amount of hydrogen in the sample was determined in the following way; the sample was placed in a container of calibrated volume and heated to 600°C. This is sufficient to drive out essentially all the hydrogen which achieved a pressure of approximately 17 mm. From the hydrogen pressure and volume and the mass of the TiFe sample, we calculated a hydrogen content of approximately 0.4 at. % (± 0.04).

RESULTS

The three velocities of plane waves in an anisotropic medium are determined by the solution of the secular equation which is cubic in ρV^2 . For each wave an equivalent modulus can be defined as equal to the root. Waves propagating in an arbitrary direction are conveniently described in a rotated coordinate system $X'Y'Z'$ in which X' is the propagation direction.

In general [3], the longitudinal modulus ($M = \rho V^2$) is approximately equal to the rotated elastic constant C'_{11} with the equality being exact for certain special directions. For cubic symmetry [4], these directions are [100], [110], and [111]. In addition, the rotated elastic constant, which is a function of the true elastic constants and the direction numbers, is a simple form

$$M_{111} \approx C'_{11}(l, m, n) = C_{11} [1 - 2R\Gamma(l, m, n)]. \quad (1)$$

Here R is a ratio of elastic constants and the anisotropy ratio $A = (C_{11} - C_{12})/2C_{44}$,

$$R = 2(A - 1)C_{44}/C_{11}, \quad (2)$$

and Γ is the quadratic orientation function of the direction numbers.

$$\Gamma = (l^2 m^2 + m^2 n^2 + n^2 l^2)/(l^2 + m^2 + n^2)^2. \quad (3)$$

It has a minimum value of zero at [100] and a maximum value of 1/3 at [111] leading to the exact value of the modulus at [111].

$$M_{111} = C'_{11}(1,1,1) = (C_{11} + 2C_{12} + 4C_{44})/3. \quad (4)$$

The longitudinal modulus and the rotated elastic constant both have a relatively broad extremum at [111], and consequently small deviations in the propagation direction from [111] lead to only small changes in the modulus. This can be seen from the fractional change in C'_{11} evaluated at [111].

$$\left. \frac{dC'_{11}}{C'_{11}} \right|_{111} = \frac{-2Rd\Gamma}{1-(2R/3)}. \quad (5)$$

The value of the fractional change as expressed in Eq. (5) depends on the deviation through Γ and the anisotropy ratio through R . Changes in Γ can be evaluated from its polar form with the result that $\pm 5.0^\circ$ deviation from [111] leads to a lowering of Γ of approximately 0.005 ($d\Gamma = -0.005$).

Tabulated [5] elastic constants for several transition metals (Cr, Fe, Ni, Nb, Ta, Mo) show that R varies between -0.6 and 0.3. Using R values in this range and the above change in Γ , the fractional change of C'_{11} can be calculated from Eq. (5). The result is ± 0.004 in the worst case. Therefore, since the deviation of the propagation direction from [111] was only 1.5° we conclude that the measured modulus is that for [111] to within 0.5%. That is, the measured modulus is the combination of elastic constants in Eq. (4) to within 0.5%.

Table 1 shows the results of absolute length and time measurements. For TiFe, using the room temperature values gives a longitudinal sound velocity of 6.339×10^5 cm/sec. Combining this value with the accepted [6] density $\rho = 6.576$ gm/cm³ gives a modulus of 2.643×10^{12} dyne/cm² as shown in Table 2. Considering errors in length and time in addition to deviation from [111], the overall error is estimated to be less than 1%.

The observed sound velocity for [111] propagation is somewhat higher than for the metals listed above, and the observed modulus is lower. Numerically, the low modulus is a direct result of the relatively low density of TiFe. Inspection of Eq. (1) shows that whether C_{11} is a maximum or minimum at [111] depends on the sign of R which in turn depends on the value of the anisotropy ratio A . Both maxima and minima occur in nature (Cr, Mo, and Nb have minima). It is possible that the relatively low modulus is associated with a minimum at [111] which would correspond to an anisotropy ratio greater than one.

Table 2 — Room-Temperature Velocity, Density, and [111] Modulus

	TiFe	TiFe + H
Velocity (cm/sec)	6.339×10^5	6.348×10^5
Density (g/cm ³)	6.576	6.576
Modulus (dyne/cm ²)	2.643×10^{12}	2.650×10^{12}

Introduction of hydrogen caused a length change of -0.22%. The observed sound velocity at room temperature is 6.348×10^5 cm/sec, an increase of 0.14%. Using the same density value gives 2.65×10^{12} dyne/cm², a 0.26% increase. If the same mass is assumed to occupy a smaller volume as a result of uniform shrinkage in all dimensions, the modulus is increased by an additional 0.66%. The fact is difficult to ascertain, since the anticipated change in diameter is 0.0003 in. and the sample is not truly cylindrical. Thus, only the first value is listed in Table 2.

Unless the thermal expansion is known it is not possible to obtain modulus values at other than room temperature. The effect of varying the temperature is to change both the path length and the density in a partially compensatory manner. Straightforward analysis shows that if l_o and t_o are the length and transit time at some reference temperature, then at some other temperature the modulus is

$$M = \rho V^2 = M_o \left(1 + \frac{\Delta t}{t_o} \right)^{-2} \left(1 + \frac{\Delta l}{l_o} \right)^{-1}. \quad (6)$$

The first two factors here are denoted the apparent modulus M_a , i.e., the modulus as uncorrected for thermal expansion.

$$M_a = M_o \left(1 + \frac{\Delta t}{t_o} \right)^{-2}. \quad (7)$$

Figure 1 is a plot of M_a vs temperature with both sets of data referenced to room temperature. Consequently Δt is always negative (Δl is expected to be) and the apparent modulus increases with decreasing temperature. Points between 77°K and 4.2°K are not plotted because of uncertainties about temperature equilibrium.

Also plotted are the estimated moduli at 4.2°K taking thermal expansion into account. This correction is estimated from comparison with other transition metals [7,8] and amounts to 0.2% in the largest case. The estimated values are 2.732×10^{12} dyne/cm² for TiFe and 2.716×10^{12} dyne/cm² for TiFe + H. Here the number of significant figures is overly reported so that the low-temperature values may be compared with the tables and graph. The modulus is not very sensitive to thermal expansion. A 100% error in estimating the change in length due to thermal expansion would raise the estimated points by another 0.2%.

No curves have been drawn through the plotted points, but it is clear that variation of the moduli would be considered normal; a roughly linear increase from room temperature followed by a flattening so as to allow the modulus to approach zero temperature with zero slope. The magnitude of the total change is within the range observed for other [5,9-11] transition metals. The steplike character of the data is thought to be an artifact which is introduced by the limit of resolution of the time measurements.

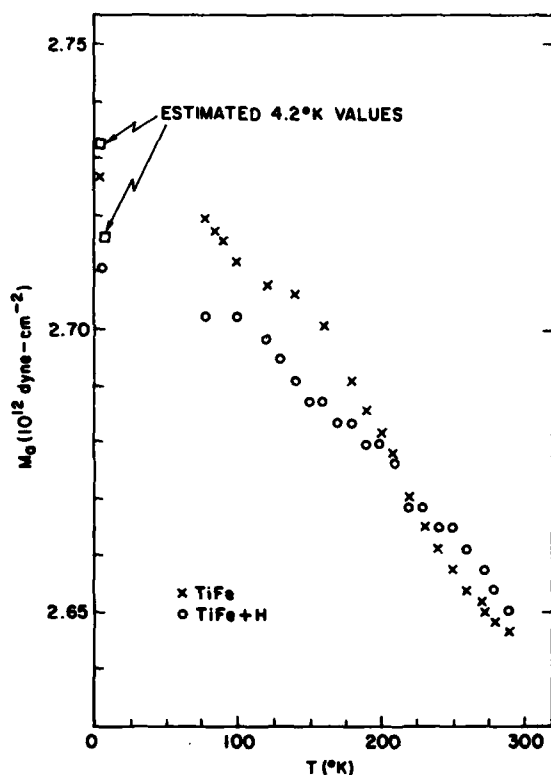


Fig. 1 — Apparent longitudinal modulus $(C_{11} + 2C_{12} + 4C_{44})/3$ as function of temperature for TiFe and TiFe + H using the measured (change) density of TiFe. The apparent moduli are referenced to room temperature for which the values of the moduli are as given in Table 2. The values at 4.2°K marked with squares are estimated to be the actual modulus including thermal expansion.

SUMMARY

The velocity of 60 MHz sound in a direction nearly parallel to [111] in single crystal TiFe was measured to be 6.339×10^5 cm/sec at room temperature. This result, combined with the rather low density gives a modulus of 2.64×10^{12} dyne/cm². Since the propagation direction was very nearly [111] and the modulus varies slowly about that direction, the measured modulus is that for [111] to within 0.5%.

Introduction of hydrogen into the crystal led to small decreases in the length and the sound pulse transit time. The combined result is a small increase (0.14%) in the room-temperature value of the sound velocity. Using the same density, we find that the resulting modulus change is twice that. If the density is assumed to change with hydrogen, the room-temperature modulus is increased by 0.9%.

Although thermal expansion data were not available, estimates of the 4.2°K values of the moduli can be made. These estimates are plotted on the graph and appear to be not unreasonable. Since the thermal expansion effect is small, large errors in the estimates would lead to only small changes in the modulus. The actual 4.2°K values probably lie between those plotted. Temperature variation of the moduli uncorrected for thermal expansion is roughly the same in both cases and about the same as for other metals.

For both experiments (with and without hydrogen) the points for a given temperature are within 0.5% of each other except for the 140°, 77°, and 4.2° points. This fact, along with consideration of all the uncertainties leads to the conclusion that the effect of hydrogen on the [111] longitudinal modulus is relatively small.

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