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Ultrasonic Attenuation and Velocity Measurements in Commercially Pure Titanium Before and After Treating in Hydrogen

By

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Abstract

The ultrasonic attenuation of commercially pure titanium and the velocity of propagation of ultrasound in it were measured at frequencies ranging from 10 to 50 mc. The same material was then heated in hydrogen for many hours at temperatures not higher than 550°C. The two ultrasonic quantities were again measured and were found to have changed remarkably especially when the metal had been heated at temperatures close to 550°C. In the latter case, long heavy lines appeared in the microstructures of the metal on heating. On being heated in hydrogen, the weight of the metal sample increased, but the size of the sample increased by a larger percentage; consequently, the density of the metal decreased, again remarkably when the sample had been heated in hydrogen close to 550°C. From the increase in weight, the hydrogen content of the sample was estimated. One sample was also outgassed after being charged with hydrogen.

To determine the effect of heating alone, samples of the metal were heated respectively in vacuum, oxygen, and nitrogen under similar conditions. No large changes in the attenuation, the velocity, and the microstructures were observed.

The changes induced by the heating in hydrogen were believed to be resulted from the appearance of new titanium-hydrogen phases. In the case of small hydrogen content, hydrogen in solution may also have an effect.

Contents

Ultrasonic Attenuation and Velocity Measurements in Commercially Pure Titanium Before and After Treating in Hydrogen

I. INTRODUCTION

To investigate the effect of occlusion of gases on the ultrasonic properties of solids, titanium and hydrogen were chosen as objects of the present study. The metal is known to be capable of absorbing the gas in a large quantity[1,2,3]. According to Hägg[2], titanium dissolves hydrogen up to 33 atomic percent, while titanium absorbing from 50 to 67 atomic percent of hydrogen forms a beta phase which has a face-centered cubic structure in contrast to the closely packed hexagonal structure of the alpha phase. These findings were generally accepted until recently[4].

Attenuation, as well as the velocity of propagation, of ultrasound in titanium, either pure or charged with hydrogen, were determined in the present study. The methods for measuring these quantities were described elsewhere[5]. The frequency of ultrasound ranges from 10 to 50 megacycles.

In order to charge titanium with hydrogen, it was found necessary to heat the metal in the gas. Since heating usually changes the microstructure of a metal and since the ultrasonic properties depend on the microstructure, notably the grain size[6], the effect of occlusion of hydrogen may not be inferred from a simple comparison of ultrasonic data obtained before and after the heating. If, however, the temperature at which the hydrogen is introduced is not very high, e.g., not higher than its recrystallization temperature, the structure of the metal may not change appreciably, if at all. An examination of microstructures can settle this point and this was done in the present experiment. Even if the structure does change, this change can be made use of in the interpretation of the ultrasonic data. In the present case of heating titanium in hydrogen, it was found that, while under certain conditions, the structure did not change appreciably, under other conditions it did change drastically. Attempts were made to charge titanium with hydrogen at room temperature by cathodic charging[8], but so far it has not been possible by this process to force a sufficient amount of gas into the interior of a sample large enough to be used for ultrasonic measurements.

Metallography was also employed in an attempt to reveal the progress of diffusion of hydrogen into titanium. Titanium samples were cut traversly after being heated in hydrogen for various lengths of time, and their cross-sections were examined under a microscope. Corresponding ultrasonic measurements were simultaneously made in some cases.

II. SOURCE, COMPOSITION, AND PREPARATION OF SAMPLES

All the samples studied were cut from two hot-rolled commercially pure rods obtained from Titanium Metals Corporation of America. These rods were designated as grade Ti-75A and had the following nominal composition:

Fe	0.10 pct.
N	0.02 pct.
O	trace
C	0.04 pct.
W	0.03 pct.
Ti	balance

One rod, which was 2" in diameter, was analyzed for the following impurities, the rest being undetermined:

Fe	0.26 pct.
N	0.060 pct.
C	0.047 pct.

This rod was supposed to have been annealed after being hot-rolled. The other rod had a diameter of 2¼" and was not analyzed. These two rods were not received at the same time.

Samples of approximately ½" in thickness were sawed off from either one of these rods. Requirements for reliable ultrasonic measurements demand that the two end faces of each sample be accurately parallel to each other. Furthermore, these surfaces should be mechanically disturbed as little as possible. For these reasons, the end faces of the samples were first faced on a lathe, then ground with a silicon carbide wheel, and finally polished on silicon carbide papers, up to grit 600, followed by a cloth on a revolving wheel with 1 micron aluminum oxide as abrasive. Samples which were to be examined for their microstructures were further polished, or alternatively etched and polished. The thicknesses of these samples were usually maintained uniform to within 2 or 3 thousandths of an inch over a large central part. Whenever the parellelism of the opposing faces of a certain sample degenerated after some treatments, the sample was ground over again.

III. EXPERIMENTAL ARRANGEMENTS

To be charged with hydrogen, titanium samples were heated in either one of two furnaces through which hydrogen was passed. At the inlets, the hydrogen was under a slight pressure of approximately 2 psi above the atmospheric pressure while at the outlets, which had small orifices, the gas was burned. The hydrogen used was that from commercial hydrogen tanks. All the samples, which were heated without frequent interruption, specifically, samples Ti506, Ti507, and Ti508, to be described below, were heated in a furnace which is used in this laboratory for growing single crystals. This furnace, referred to later as Furnace A, was always heated up or cooled down slowly, i.e. in a few hours. The required elevated temperatures were generally maintained constant to within ± 10°C. The other furnace, referred to later as Furnace B, was a commercial hydrogen atmosphere furnace, equipped with a cooling chamber and a quenching outlet. Samples could be heated up or cooled down within minutes or seconds. While samples heated in the first furnace always appeared grayish, samples heated in the second furnace had bluish or purple appearances. These films were usually not thicker than 1 or 2 thousandths of an inch. The temperature of the second furnace was controlled by a commercial vane type millivolt controller.

Samples were also heated in nitrogen, oxygen, and vacuum respectively, mainly to determine the effect of heating alone, or of heating in the presence of some gases other than hydrogen.

A large closed metal system with an oil diffusion pump backed by a mechanical pump was used for the vacuum heating. The heating element was inside the closed system, the pressure in which could be reduced to not more than a few microns of mercury. For heating in oxygen, the sample was sealed into a small gas-tight metal chamber, which was flushed and filled with oxygen. The chamber was then heated in a furnace. During heating, the pressure inside the chamber was found to be much higher than the atmospheric pressure. For heating in nitrogen, the same furnace, built for growing single crystals as mentioned above, was used. The gas inlet was connected to a nitrogen tank regulated at about 5 psi above the atmospheric pressure. The valve controlling the gas outlet was closed after an initial flushing. Since the furnace is fairly but not completely tight, it is not known how pure the nitrogen gas was inside the furnace during heating. However, since the main purpose of this heat treatment was to determine the effect of heating titanium in the absence of large concentration of hydrogen, no careful determination was made about the purity of this particular gas atmosphere. This heat treatment will be referred to in what follows as heating in nitrogen.

For the measurements of attenuation and velocity of propagation of ultrasound in titanium, the arrangement developed by Roderick and Truell[5] was used with some slight modification. In the arrangement of Roderick and Truell, the maximum amplitudes of individual echoes were measured by comparing them with those of pulses of known attenuation generated by a separate transmitter. In the present experiment, the attenuation was measured in part by a simplifying arrangement*. Since the maximum amplitudes of a series of echoes are expected to decrease exponentially[5], an exponential curve of variable decay constant was superposed onto the oscilloscope screen on which the echoes were seen. By varying a resistance in the circuit of the generator which produced this exponential curve, the decay constant of the curve could be so adjusted that the curve fit the tops of any particular series of echoes. The exponential curve had been calibrated with the use of pulses of known attenuation. Therefore, in accordance with the value of the resistance, the value of attenuation for this series of echoes could be read directly from a calibration chart.

In the metallographic work, either hydrofluoric acid in glycerine or some mixture of this acid and nitric acid in glycerine or water was used for etching. A table microscope fitted with a regular camera was used for taking photographs.

In heating titanium in hydrogen, it was found that the volumes and weights of titanium samples changed by an appreciable amount under certain conditions. Accordingly, these quantities were generally measured, with a micrometer to 10^{-4}" and a balance to 10^{-1} mg respectively. From these

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*Developed in this laboratory. Details to be published.

values, the densities of these samples at different stages could be computed. Since the dimensions of the samples were generally uniform to a few thousandths of an inch, these density values should be significant to three digits, each sample being as thick as about ½" and weighing more than 100 gm. Changes in densities were found to be large, 10 percent in one case. For some practical reason, hydrostatic weighing was not attempted in addition.

IV. EXPERIMENTAL RESULTS

A total of 10 samples was studied, in addition to a few samples investigated during preliminary runs. The sources and the treatment before and during study of these samples are listed in Table I. Samples were numbered in the order as they were cut from the rods; henc, samples which had consecutive numbers were adjacent to each other in a given rod. Such adjacent samples should have similar mechanical and chemical properties before heat treatment. Some samples were heated in vacuum in groups, before any study of them was started, so that they were annealed and partially outgassed.

Results on the attenuation of these samples are plotted in Figs. 1 - 7. In these figures the energy loss of ultrasound in db per inch of the metal, treated or untreated, is given as a function of the frequency of ultrasound. In Fig. 3,

Table I

Heat Treatment of Titanium Samples

Sample	Source	Treatment before study	Treatment during study			
			Order	Atmosphere	Temperature (°C)	Length of time (hr)
T1507	2¼"rod	Heated together in vacuum at approximately 750°C for 4 hours.		H_2	440	66
T1506	2¼"rod		1st	H_2	500	77
			2nd	H_2	460	50
			3rd	H_2	500	65
T1508	2¼"rod		1st	H_2	550	44
			2nd	H_2	550	61
			3rd	Vacuum	550	24
			4th	Vacuum	550	37
					590	3
T1514	2" rod					
T1513	2" rod	"	1st -11th	H_2	550	114
T1512	2" rod			H_2	550	61
T1515	2" rod			Vacuum	550	74
T1520	2" rod			Vacuum	590	77
T1503	2¼"rod			N_2	600	45
T1505	2¼"rod			O_2	600	71

the results of attenuation measurements of T1508 after the sample was heated for the second time in hydrogen are not given. These results will be mentioned later.

Results on the velocity of propagation are given in Table II. Velocities were usually measured for several frequencies. No systematic dependence of velocity values on frequency was noticed in the investigated frequency range of 10 to 50 mc within the accuracy of measurement. Therefore, the values of velocity were averaged over the frequency range for each sample at each stage.

Changes of weights and volumes of samples during some heat treatments were measured for some samples. Data for these samples are given in Tables III and IV. It will be noted that

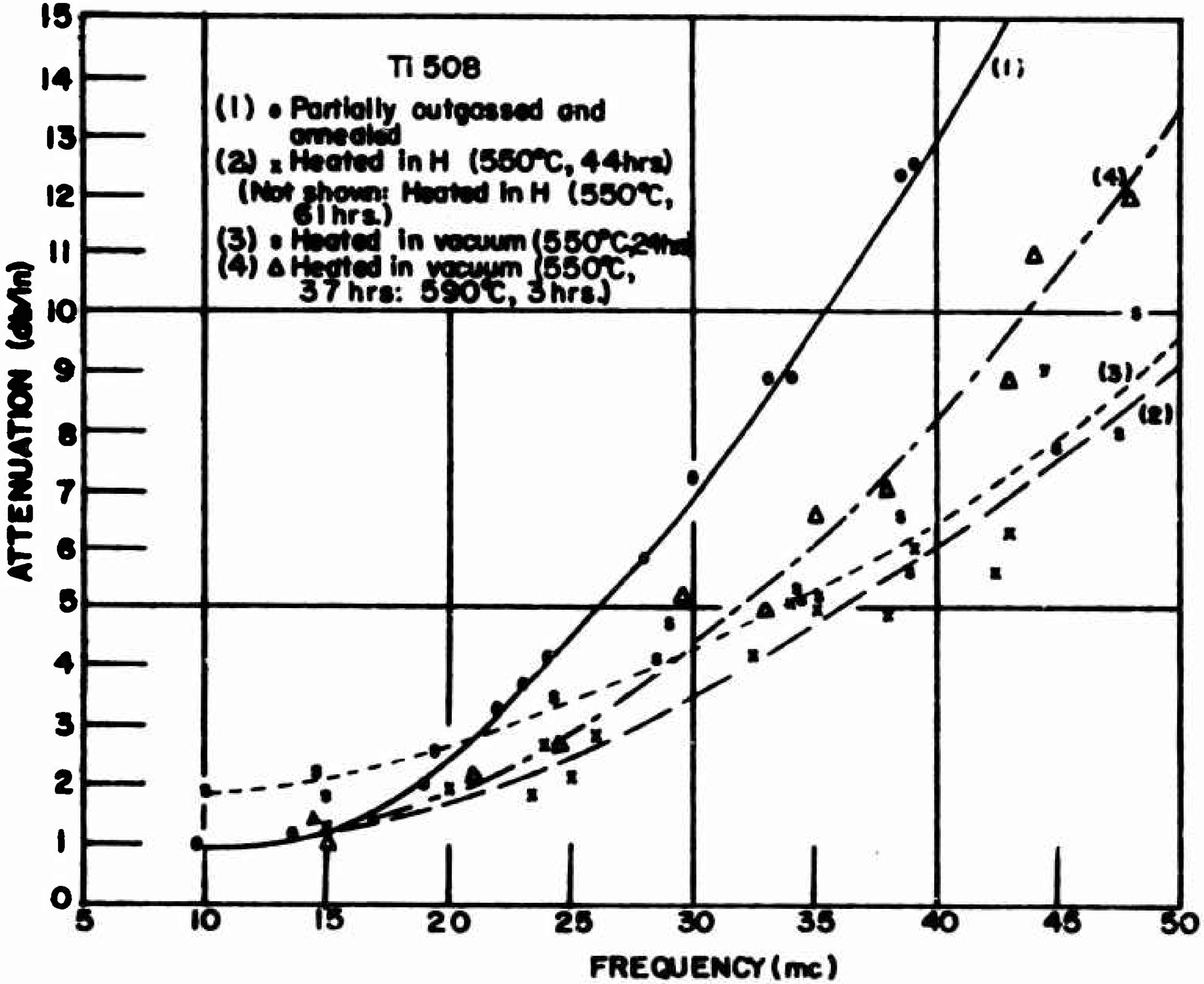


FIG. I. ATTENUATION-FREQUENCY PLOT FOR TI 508

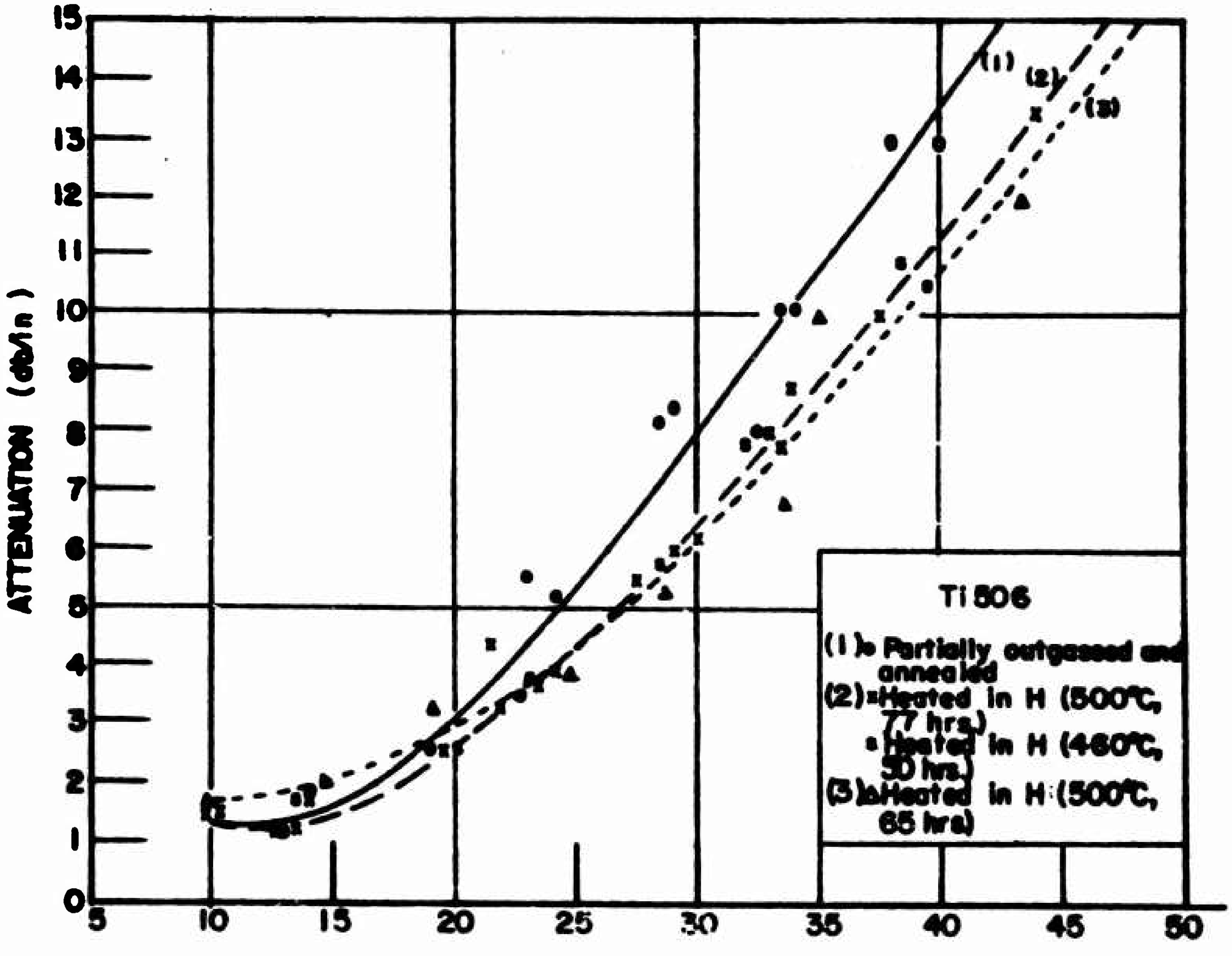


FIG. 2. ATTENUATION-FREQUENCY PLOT FOR Ti 506

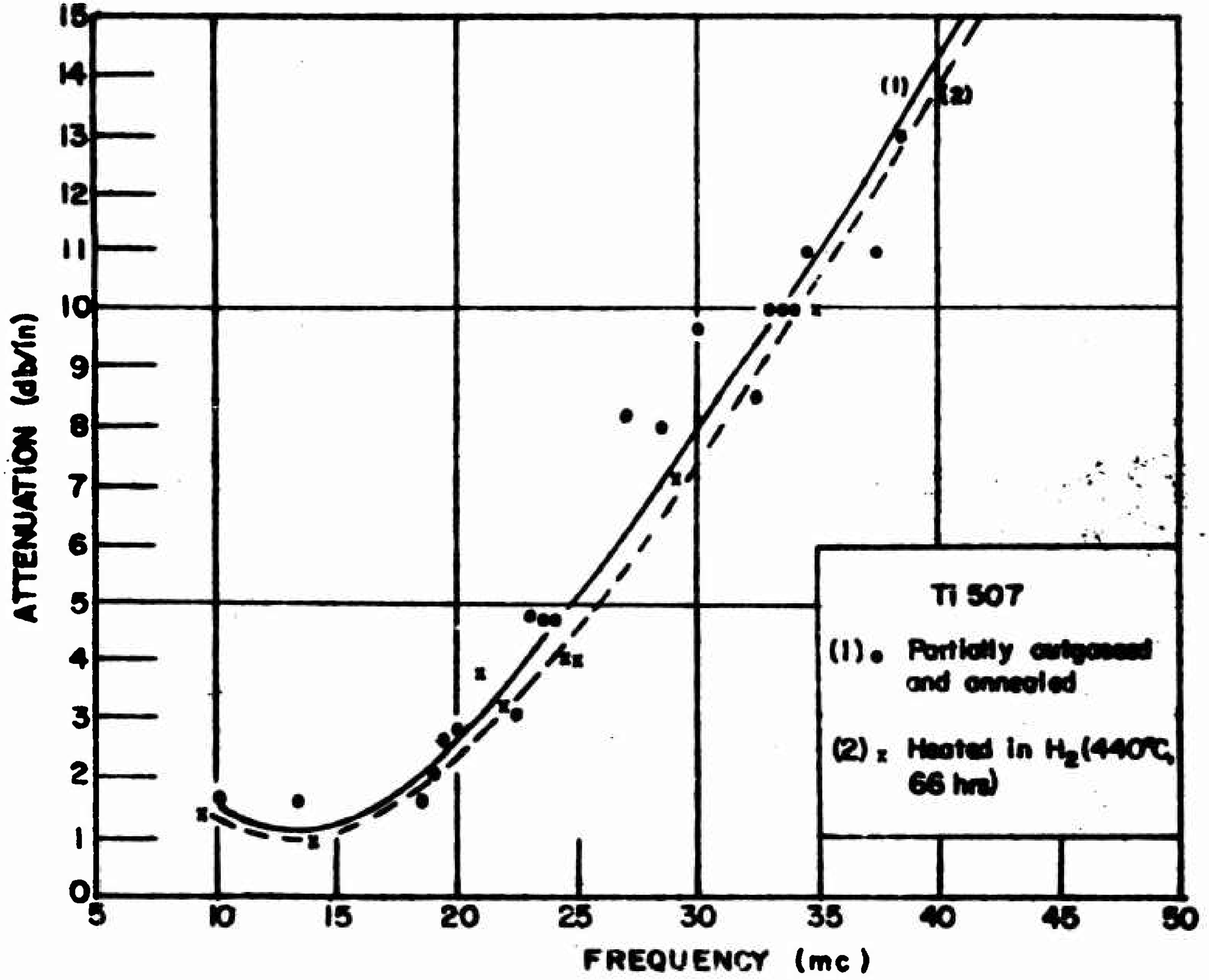


FIG. 3. ATTENUATION - FREQUENCY PLOT FOR Ti 507

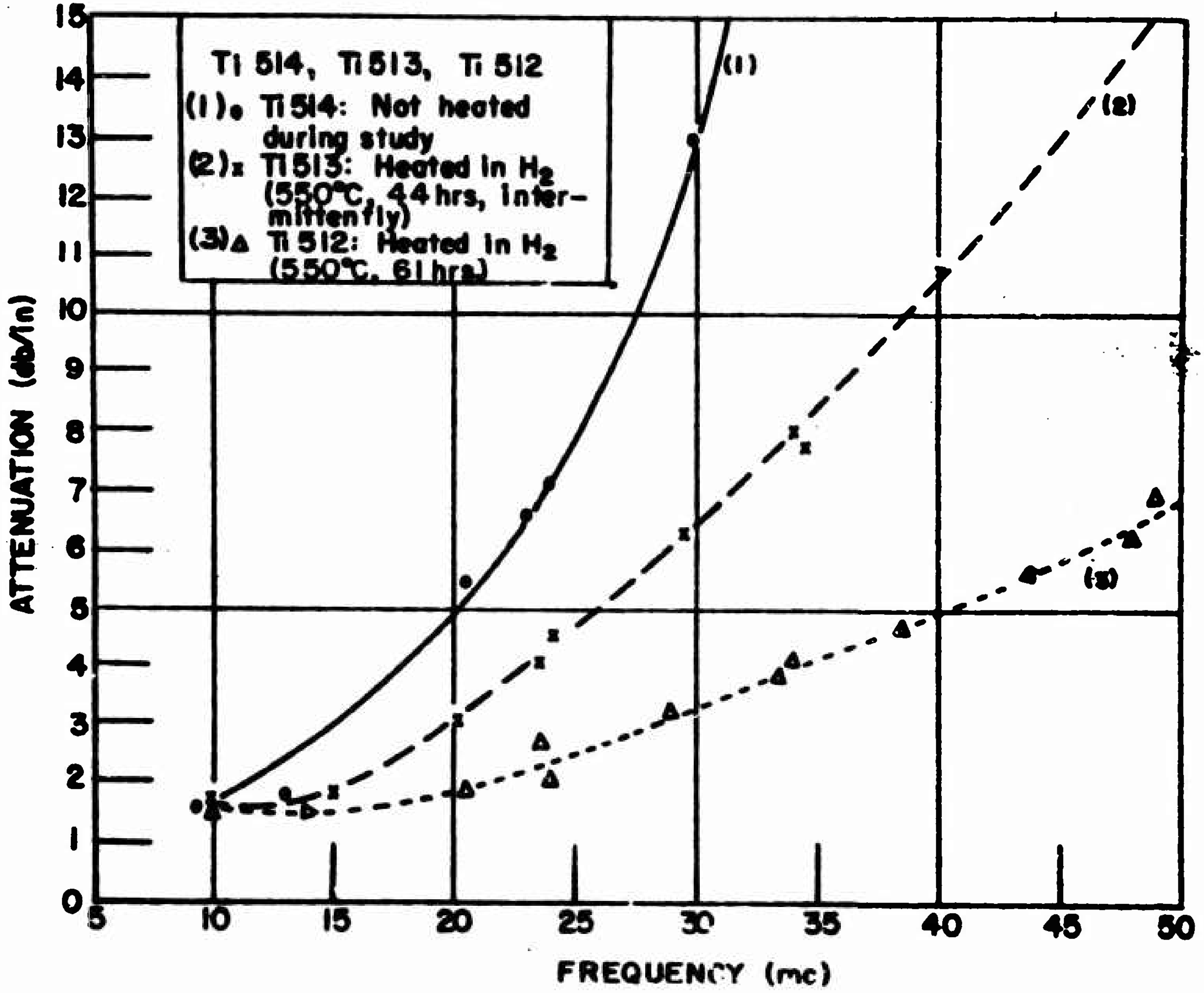


FIG. 4. ATTENUATION – FREQUENCY PLOT FOR Ti514, Ti513, AND Ti512

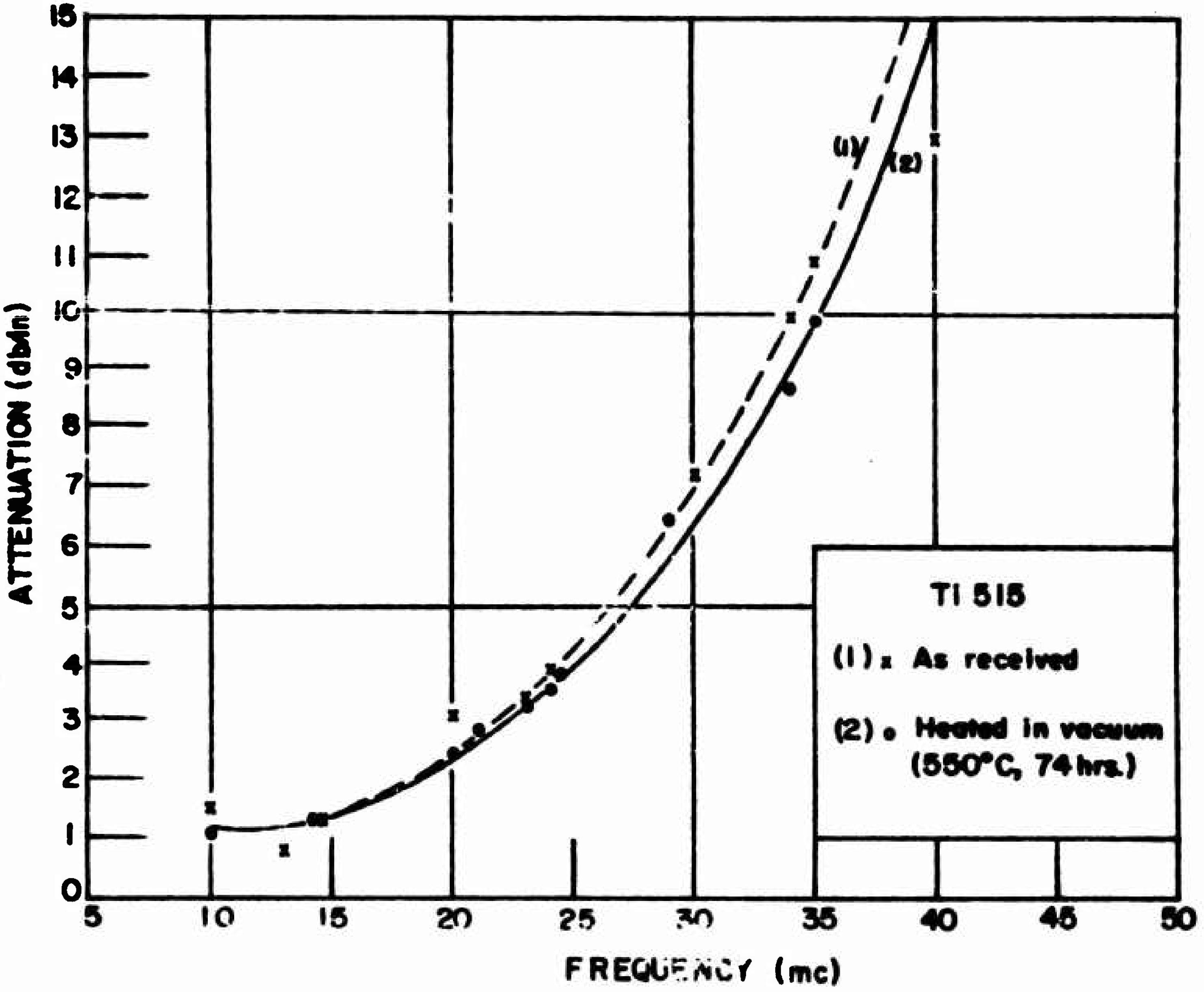


FIG. 5(a) ATTENUATION - FREQUENCY PLOT FOR TI 515

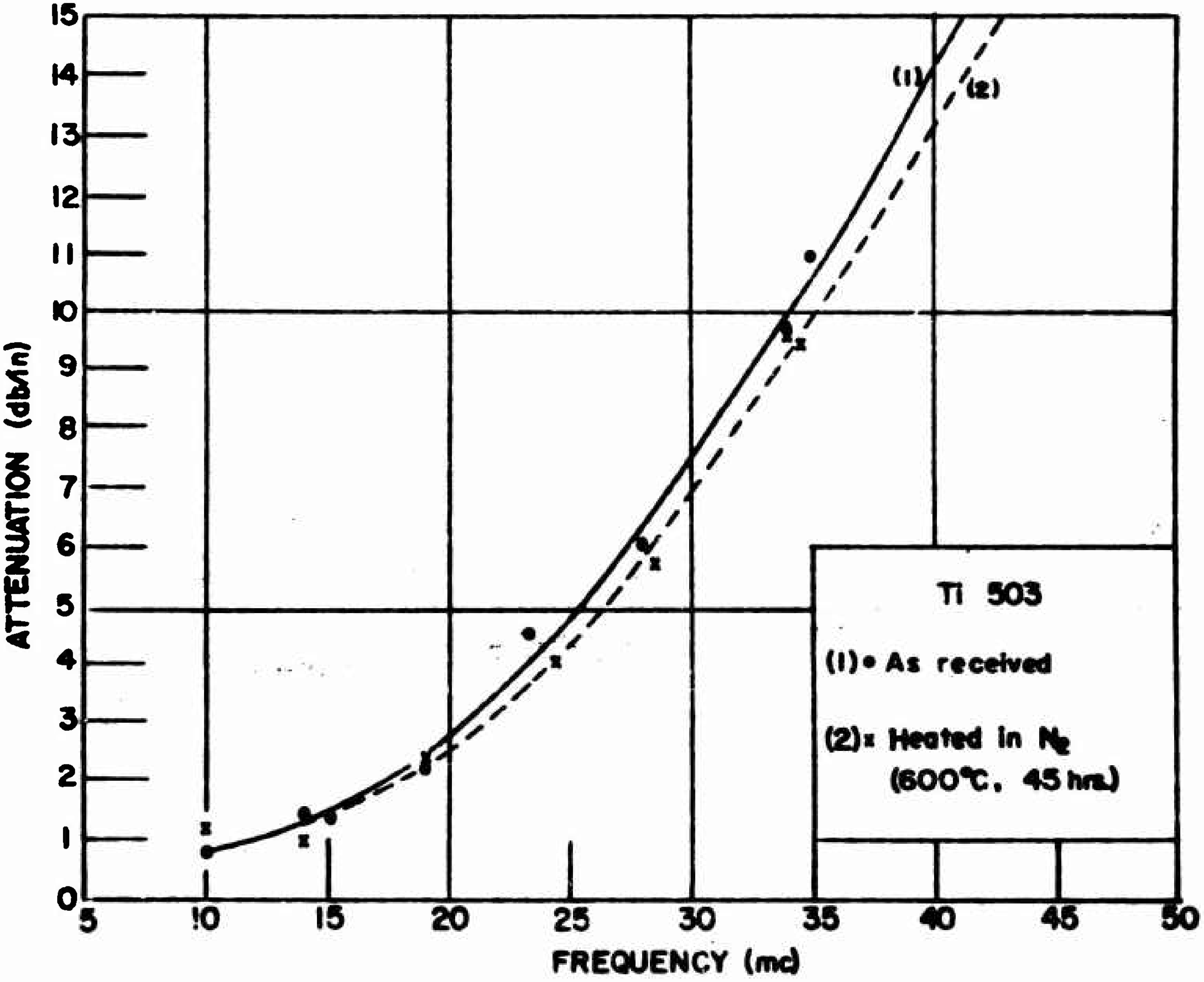


FIG 6. ATTENUATION–FREQUENCY PLOT FOR TI503

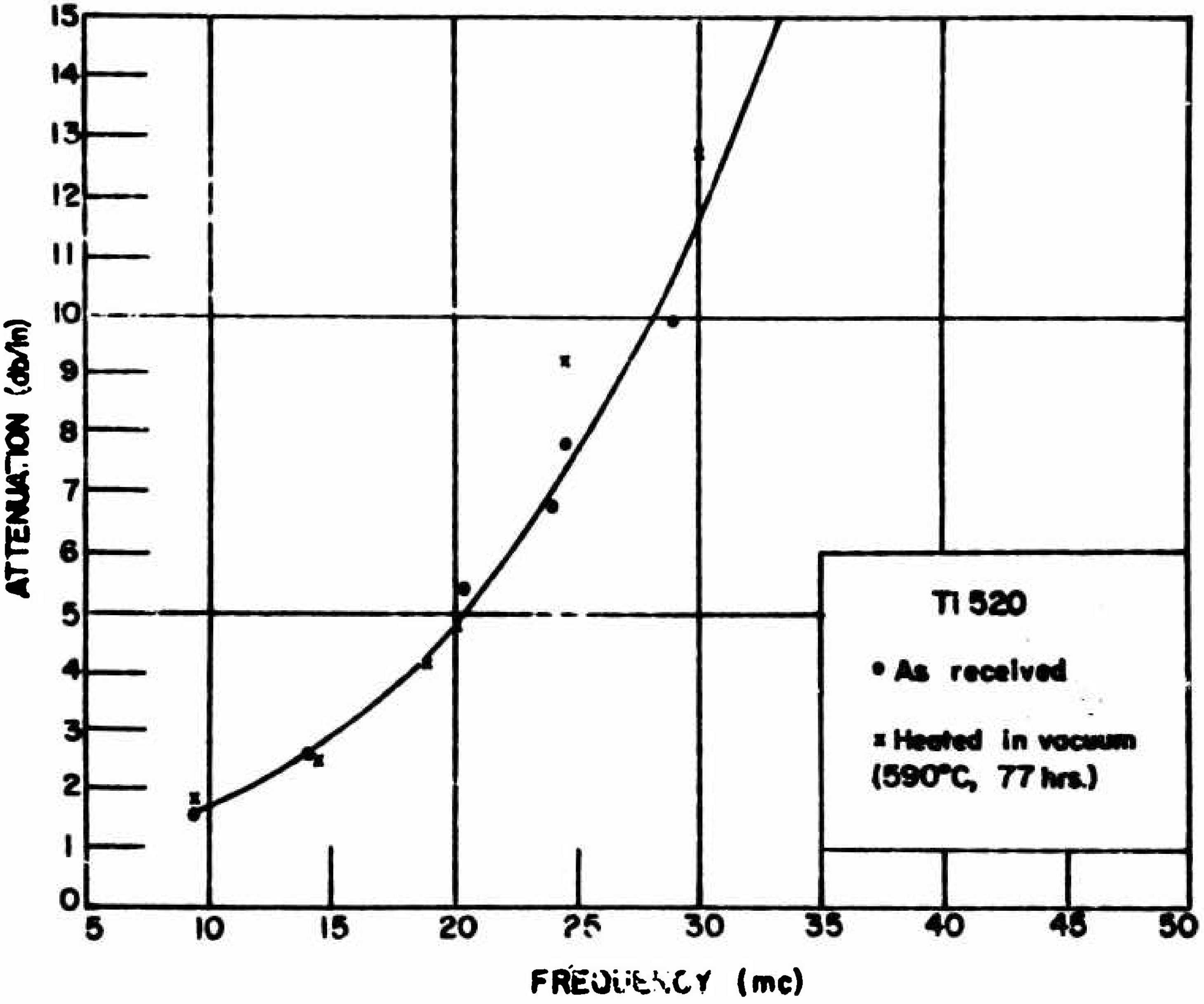


FIG. 5(b) ATTENUATION - FREQUENCY PLOT FOR TI 520

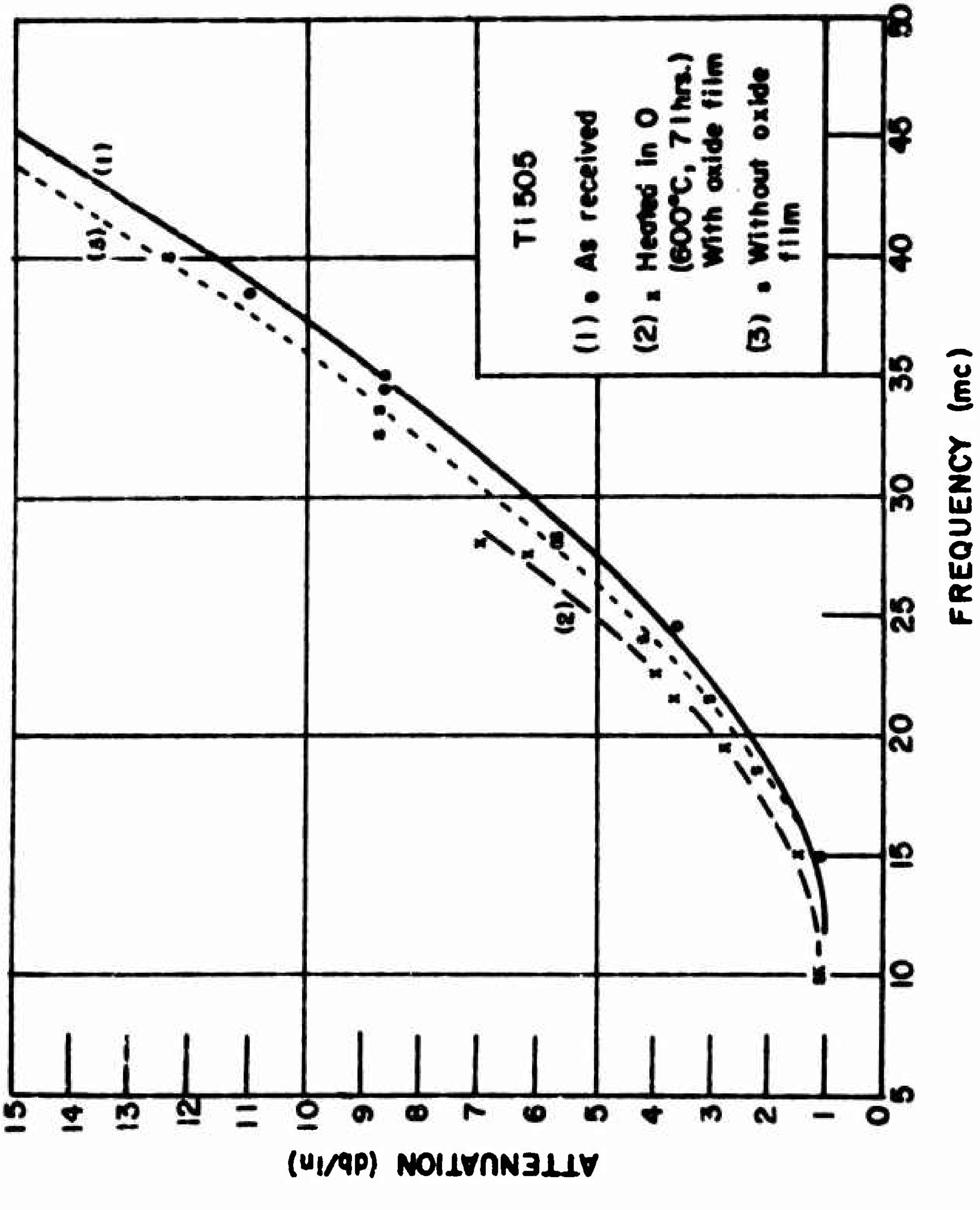


FIG. 7. ATTENUATION-FREQUENCY PLOT FOR Ti 505

Table II

Values of velocity of propagation in titanium samples for frequencies from 10 up to 50 mc

Sample	Treatment (Details given in Table I)	Velocity (in 10^5 cm/sec)
Ti507	Vacuum annealed and outgassed	5.85
	Heated in H_2	5.88
Ti506	Vacuum annealed and outgassed	5.83
	1st heating (H_2)	5.88
	2nd heating (H_2)	5.96
	3rd heating (H_2)	5.96
Ti508	Vacuum annealed and outgassed	5.87
	1st heating (H_2)	6.32
	2nd heating (H_2)	6.52
	3rd heating (vacuum)	6.11
	4th heating (vacuum)	5.94
Ti514	Vacuum annealed and outgassed	5.89
Ti513	7th heating (H_2)	6.04
	11th heating (H_2)	6.04
Ti512	Heated in H_2	6.13
Ti515	As received	5.93
	Heated in vacuum	5.91
Ti520	As received	5.86
	Heated in vacuum	5.93
Ti503	As received	not determined
	Heated in N_2	5.90
Ti505	As received	not determined
	Heated in O_2 (film remaining)	5.95
	(film polished off)	5.96

for some samples, notably Ti508, the changes were tremendous. From the measured weights and volumes, the densities of these samples are computed and listed in one of the tables. From the gains in weight during heating in hydrogen, of the losses during heating in vacuum after samples were charged with hydrogen, the amounts of hydrogen introduced or expelled are computed and listed. Computations are based on the assumption that all changes in weight are caused by hydrogen alone. While

Table III

Dimensions and Weights of Ti507, Ti506, and Ti508
Before and After Various Treatments

Sample	Treatment	Occasion	Measured			Computed		
			Thickness (cm)	Diameter (cm)	Weight (gm)	Volume (cm^3)	Density (gm/cm^3)	Hydrogen Content (atomic percent)
Ti507	Heated in H_2 (440°C, 66 hours)	Before heating	1.344	5.7226	151.8082	34.1	4.46	0
		After heating	1.343	5.7307	151.9098	34.1	4.45	3.08
		Increase: Actual	-0.001	0.0081	0.1016	$<.1$	-0.01	3.08
		Percentage	$-7x10^{-2}$	$1x10^{-1}$	$7x10^{-2}$	$<3x10^{-1}$	$-2x10^{-1}$	
Ti506	Heated for the first time in H_2 (500°C, 77 hours)	Before heating	1.460	5.7170	164.6702	36.5	4.51	0
		After heating	1.464	5.7437	164.9800	37.0	4.46	8.20
		Increase: Actual	0.004	0.267	0.3098	0.5	-0.05	8.20
		Percentage	$3x10^{-1}$	$5x10^{-1}$	$2x10^{-1}$	1	-1	
	Heated for the second time in H_2 (460°C, 50 hours)	Before heating	1.451	5.7437	163.7468	36.6	4.47	8.20
		After heating	1.453	5.7556	163.8886	36.8	4.45	11.6
		Increase: Actual	0.002	0.0119	0.1418	0.2	-0.02	3.4
		Percentage	$1x10^{-1}$	$2x10^{-1}$	$9x10^{-2}$	$5x10^{-1}$	$-4x10^{-1}$	
	Heated for the third time in H_2 (500°C, 65 hours)	Before heating	1.451	5.7556	163.6810	36.7	4.46	11.6
		After heating	1.452	5.7648	163.7918	36.9	4.44	14.0
		Increase: Actual	0.001	0.0092	0.1108	0.2	-0.02	2.4
		Percentage	$7x10^{-2}$	$2x10^{-1}$	$7x10^{-2}$	$5x10^{-1}$	$-4x10^{-1}$	

Continued on the next page.

Continuation of Table III

Sample	Treatment	Occasion	Measured			Computed		
			Thickness (cm)	Diameter (cm)	Weight (gm)	Volume (cm^3)	Density (gm/cm^3)	Hydrogen Content (atomic percent)
T1508	Heated in H_2 (550°C, 44 hours)	Before heating	1.273	5.7160	142.8108	31.6	4.51	0
		After heating	1.321	5.8986	145.2278	34.8	4.18	44.4
		Increase: Actual	0.048	0.1826	2.4170	3.2	-0.33	44.4
		Percentage	3.8	3.2	1.7	10	-7.3	
	Heated again in H_2 (550°C, 61 hours)	Before heating	1.294	5.8953	142.0960	34.2	4.16	44.4
		After heating	1.310	5.9990	143.4499	35.8	4.00	55.8
		Increase: Actual	0.016	0.1037	1.3539	1.6	-0.16	11.4
		Percentage	1.2	1.8	1.0	4.7	-3.8	
	Heated in vacuum (550°C, 24 hours)	Before heating	1.296	5.9954	141.6689	35.4	4.00	55.8
		After heating	1.249	5.8125	139.2096	32.1	4.34	29.1
		Increase: Actual	-0.047	-0.1829	-2.4593	-3.3	0.34	-26.7
		Percentage	-3.6	-3.1	-1.7	-9.3	8.5	
	Heated again in vacuum (550°C, 37 hours; 590°C, 3 hours)	Before heating	1.230	5.8034	137.0226	31.4	4.36	29.1
		After heating	1.212	5.7351	136.1450	30.2	4.50	9.42
		Increase: Actual	-0.018	-0.0683	-0.877[illegible]	-1.2	0.14	-19.7
		Percentage	-1.5	-1.2	-0.6	-3.8	3.2	

Table IV

Dimensions and Weights of Ti505, Ti515,
and Ti520 Before and After Treatment

Sample	Treatment	Occasion	Thickness (inch)	Diameter (inch)	Weight (gram)
Ti505	Heated in O_2 (600°C, 60 hours)	Before heating	0.4602	2.2530	132.3030
		After heating	0.4611	$>$2.2531 $<$ 2.2540	132.3970
Ti515	Heated in vacuum (550°C, 74 hours)	Before heating	0.5622	2.2526	160.9540
		After heating	0.5625	2.2518	160.9498
Ti520	Heated in vacuum (590°C, 78 hours)	Before heating	0.5222	1.9984	117.9318
		After heating	0.5223	1.9986	117.9330

the hydrogen used was not purified, this assumption is considered sufficiently valid for the following reasons: From Table IV it is evident that titanium samples did not gain appreciable weight when they were heated in commercial oxygen at about the same temperature as in commercial hydrogen. Therefore, any oxygen present in commercial hydrogen as an impurity, or any other gaseous impurities common to both commercial hydrogen and commercial oxygen were not responsible for significant changes in weight. Similar data on nitrogen was unfortunately not obtained, because Ti503 had been heated in nitrogen before large changes in weight of samples heated in hydrogen were noticed. Nevertheless, the value of its density after heating, which was 4.50 gm/cc, suggests that at most a small amount of weight was gained during heating.

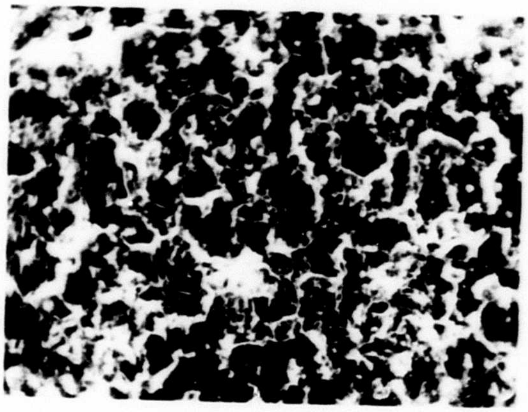
Surfaces of samples heated in hydrogen did not have the same appearance after heating as before it. The films which appeared, whether they were composed entirely of hydrides or not, were, as mentioned earlier, rather thin, of the order of a few thousandths of an inch. Densities of some samples, which underwent large changes in weight, were determined both before and after the films were polished off. Their values did not differ. In the case of Ti508, the sample lost a large amount of weight during heating in vacuum, even though its surfaces had been polished before heating. While this sample was being heated, for the first time in vacuum after it had been heated in hydrogen, the pressure of the vacuum system stayed for several hours at the value of about a hundred microns of mercury. On the other hand, when other samples were similarly heated, which had not been heated in hydrogen before, the pressure did not reach higher than a few microns all the time. For these and other reasons, it can be concluded that large changes in weight were not caused by any reaction of sample surfaces with some impurities in hydrogen.

In spite of the above mentioned facts it is to be expected that the computed values of hydrogen content given in Table III were only approximate at best. For this reason, the hydrogen content in the as-received samples is indicated as zero in the table although in actuality, these samples were most likely not entirely hydrogen free.

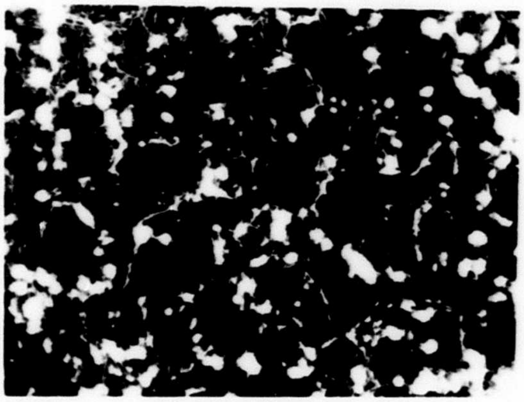
After every heat treatment, the microstructures of the samples listed in Table I were generally examined. Photomicrographs of most of these samples after various treatments are shown in Figs. 8 - 12. Photographs of a few samples before they were ever heated in any gas are not presented, because the samples were then not studied. In these cases, photographs of adjacent samples are used as substitutes. For example, Ti502 was cut from the 2¼" rod next to Ti503 and was never heated. A photomicrograph of this sample is then presented together with photomicrographs of heated Ti503 and heated Ti505 (Fig. 12). Similarly, Ti516 and Ti521 were photographed in their as-received form (Fig. 11).

V. DISCUSSIONS

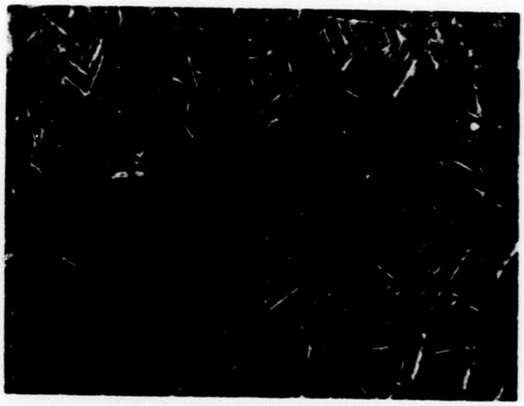
It was established in this experiment that commercially pure titanium, on being heated in hydrogen under certain conditions, changes its ultrasonic properties as well as its density. While it was intended to study only the effect of occlusion of hydrogen by the metal when the experiment started, metallographic observations during this experiment indicated that in some cases, hydrogen was not all in solution and some other effect was involved. In the meantime, other workers reported[4] similar metallographic findings, with the conclusion that titanium hydride is produced even when only a small amount of hydrogen is absorbed by the titanium. This does not necessarily imply that no hydrogen can be in solution.



(a) Partially outgassed and annealed.



(b) Heated for the first time in hydrogen ($550^{\circ}C$, 44 hrs)



(c) Heated for the second time in hydrogen ($550^{\circ}C$, 61 hrs)

Fig. 8
Photomicrographs of Ti508 (320x)

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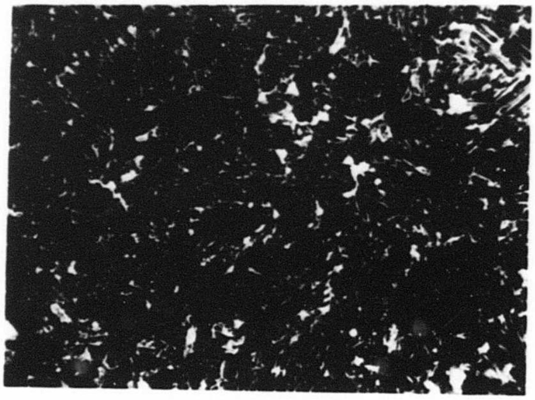
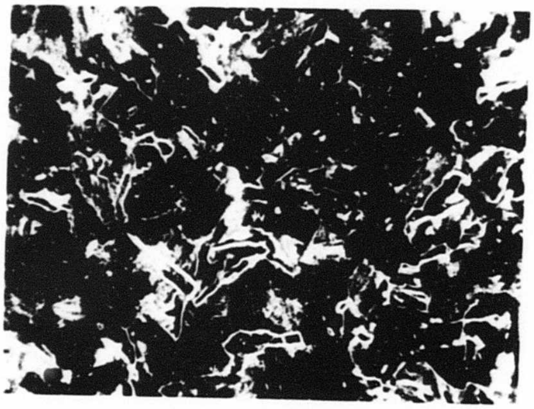
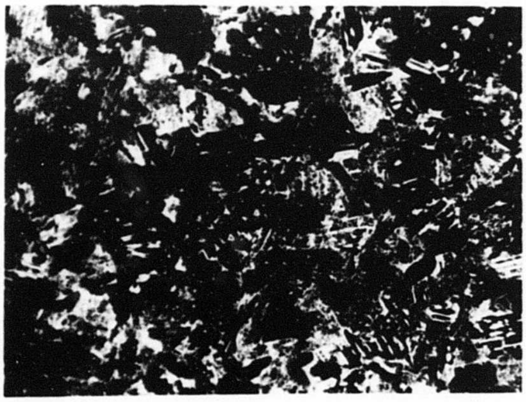


(d) Heated for the first time in vacuum (after being heated in hydrogen)
(550°C, 24 hrs)

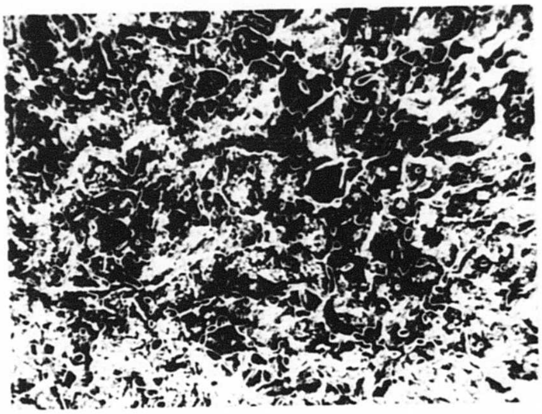


(e) Heated for the second time in vacuum
(550°C, 37 hrs:
590°C, 3 hrs)

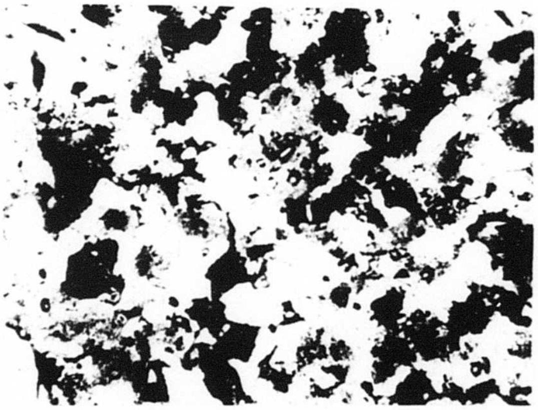


(f) Heated for the third time in vacuum
(600°C, 40 hrs)
(This heating is not mentioned in the text.)

Continuation of Fig. 8 (320x).



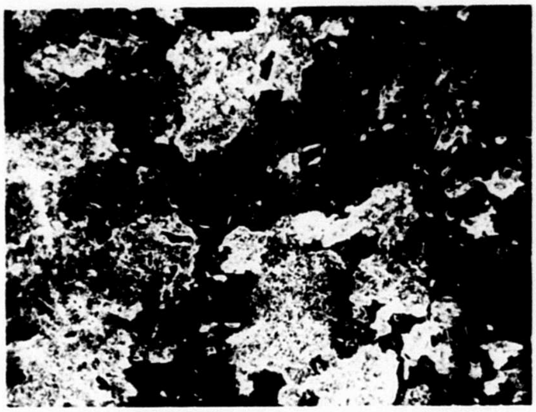
(a) Ti506 — heated in hydrogen
(500°C, 77 hrs:
460°C, 50 hrs:
500°C, 65 hrs)



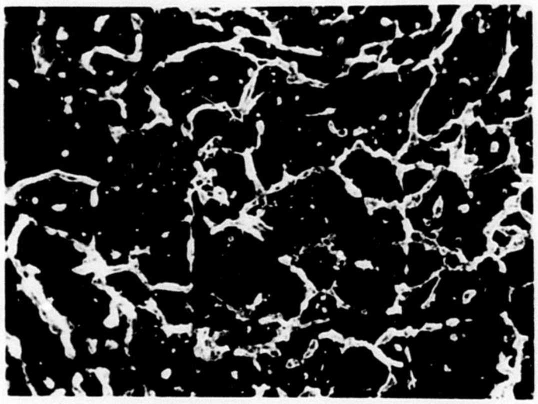
(b) Ti507 — partially outgassed
and annealed.

(c) Ti507 — heated in hydrogen
(440°C, 66 hrs)

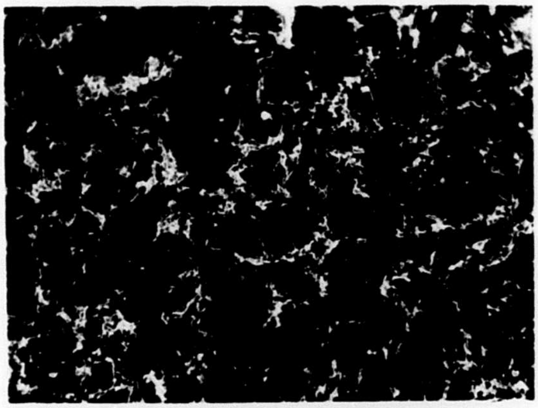
Fig. 9
Photomicrographs of Ti506 (320x)



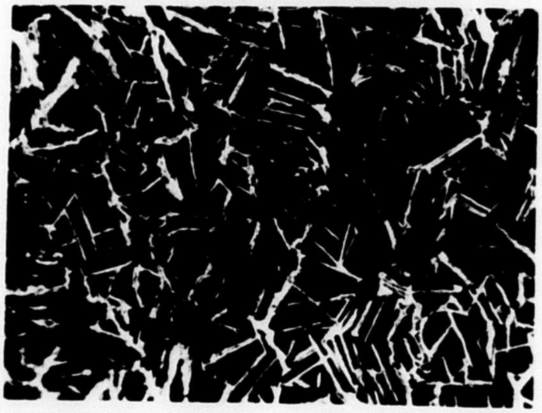
(a) Ti514 — partially outgassed and annealed.



(b) Ti513 — heated intermittently in hydrogen (550°C, 36 hrs)

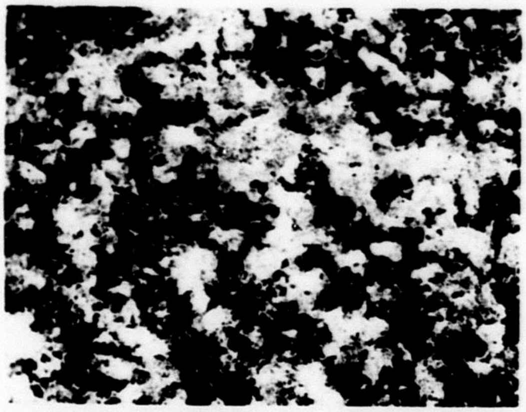


(c) Cross-section of the same sample mentioned in (b).

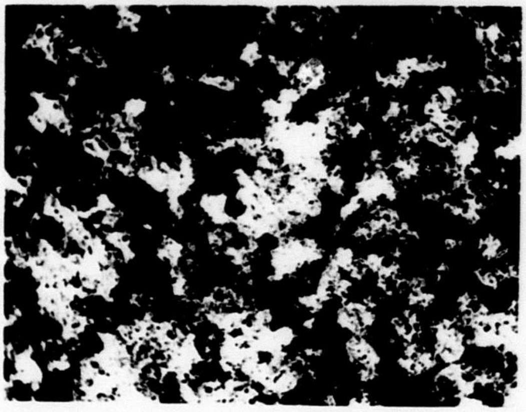


(d) Ti512 — heated in hydrogen (550°C, 61 hrs)

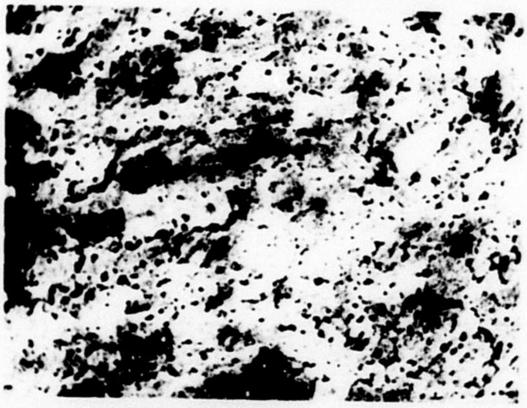
Fig. 10
Photomicrographs of Ti514,
Ti513, and Ti512 (320x)



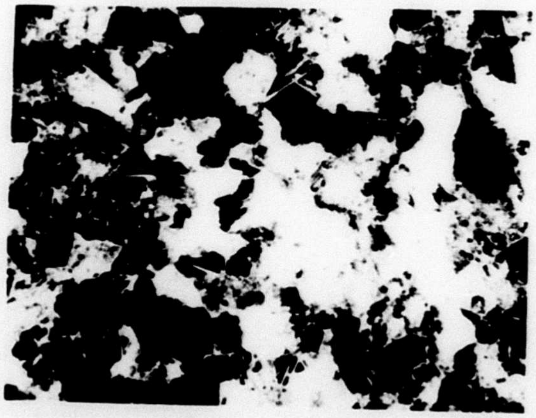
(a) Ti516 — as received



(b) Ti515 — heated in vacuum (550°C, 74 hrs)

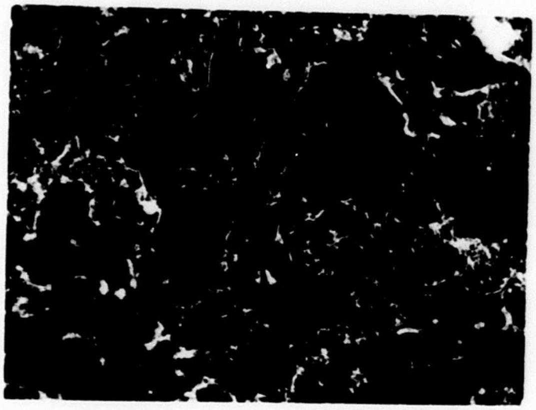


(c) Ti521 — as received

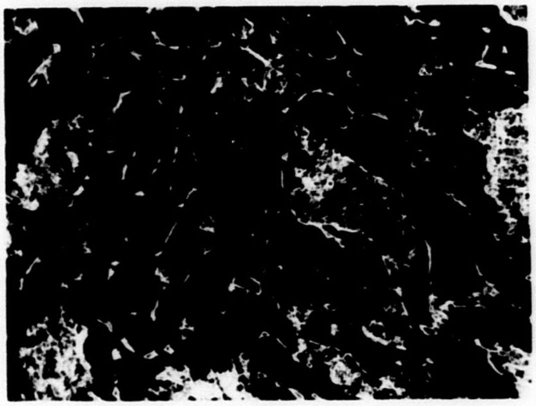


(d) Ti520 — heated in vacuum (590°C, 77 hrs)

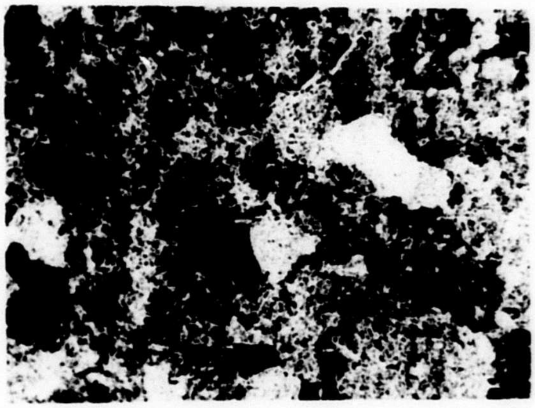
Fig. 11
Photomicrographs of Ti516, Ti515,
Ti521, and Ti520 (150x)



(a) Ti502 — as received



(b) Ti503 — heated in nitrogen
(600°C, 45 hrs)



(c) Ti505 — heated in oxygen
(600°C, 71 hrs)

Fig. 12
Photomicrographs of Ti502,
Ti503, and Ti505 (320x)

Of all the samples, Ti508 underwent one of the largest changes on being heated in hydrogen. This sample was also studied more thoroughly than some of the other samples. Data for this sample on weight, volume, density, and velocity of ultrasound, shown earlier in slightly different ways in Tables I, II, and III, are retabulated in Table V. The changes in these quantities, induced by various heat treatments, were obviously large as were the changes in the ultrasonic attenuation shown in Fig. 1. During the first heating in hydrogen, the attenuation decreased up to 70% or more. On being heated for the second time in hydrogen, the attenuation of the sample actually changed so much that the values of attenuation could no longer be measured by the present arrangement for the following reasons. It was remarked, in the section on experimental arrangements, that generally the maximum amplitudes of the series of echoes decay exponentially and this exponential decay gives a measure of attenuation. After the second heating in hydrogen, the envelope of the echoes from Ti508 did not have a smooth exponential shape, but had either a hump or a plateau near its end. When there is a large energy loss at a given point or interface in the solid, the use of an attenuation measure is no longer appropriate because the ratio of energy lost to the total amount of energy present in the pulse may be too large. Only after the sample was subsequently heated in vacuum, were the patterns of echoes regular again. From Table V and Fig. 1, it will be noticed that effects introduced by

TABLE V

Retabulation of Data on Weight, Volume, and Density of, and Velocity of Ultrasound in, Ti508

Heat treatment	Weight increase through heating (%)	Volume increase through heating (%)	$\frac{\text{Density after heating}}{\text{Density before heating}}$	$\left(\frac{\text{Density before any heating}}{\text{Density after heating}}\right)^{\frac{1}{2}}$	$\frac{\text{Velocity of ultrasound after heating}}{\text{Velocity of ultrasound before any heating}}$
Heated in H_2 (550°C, 44 hrs)	1.7	/ 1.0	$\frac{4.18}{4.51} = .927$	$\sqrt{\frac{4.51}{4.18}} = 1.04$	$\frac{6.32}{5.87} = 1.08$
Heated in H_2 (550°C, 61 hrs)	1.0	4.7	$\frac{4.00}{4.51} = .887$	$\sqrt{\frac{4.51}{4.00}} = 1.06$	$\frac{6.52}{5.87} = 1.11$
Heated in Vacuum (550°C, 24 hrs)	-1.7	-9.3	$\frac{4.34}{4.51} = .962$	$\sqrt{\frac{4.51}{4.34}} = 1.02$	$\frac{6.11}{5.87} = 1.04$
Heated in Vacuum (550°C, 37 hrs; 590°C, 3 hrs)	-0.6	-3.8	$\frac{4.50}{4.51} = .998$	$\sqrt{\frac{4.51}{4.50}} = 1.00$	$\frac{5.94}{5.87} = 1.01$

heating the sample in hydrogen were annulled, not quite for the attenuation, but almost completely for the density and the velocity, by a sufficient heating in vacuum.

On comparing the data for Ti508 with those for Ti515 and Ti520 (Fig. 5, Tables II and IV), which were heated in vacuum, and with those for Ti503 and Ti505 (Fig. 5, 6, and 7, Tables II and III), which were heated respectively in nitrogen and oxygen, it can be inferred that heating in the presence of hydrogen, not heating alone, was essential for introducing large changes in the density and ultrasonic properties of titanium. It is not to be inferred that pure heating, or heating in the presence of nitrogen and oxygen, will not change these quantities under any circumstances. It was only established that, at the relatively low temperature of 550°C, hydrogen alone could diffuse, by sufficient amount, into titanium and thus remarkably change some of its properties.

Hägg reported[2] that titanium can dissolve hydrogen up to 33 atomic percent. In this dissolved state, i.e., in the α-phase, hydrogen atoms occupy interstitial sites[7], thus expanding the lattice of titanium. These interstitial atoms may be mobile. It can reasonably be expected that their presence will affect the ultrasonic properties of the solvent.

However, Hägg also reported[2] that when the hydrogen content in titanium is larger than 33 atomic percent, a new β-phase appears. It is the appearance of this β-phase, which is believed to be primarily responsible for the large changes in the ultrasonic properties of Ti508 when it was heated in hydrogen. The hydrogen content of the sample after the first heating in hydrogen was 44 atomic percent and was beyond the region of Hagg's pure α-phase. After the second heating in the same gas, the hydrogen content was 56 atomic percent, and was in the pure β-phase region. As is evident from Fig. 8, the sample did acquire remarkably different microstructures after being heated in hydrogen.

In order to examine the effect of dissolved hydrogen, it is necessary to study samples which have small hydrogen content. After being heated in hydrogen for the first time, Ti506 had a hydrogen content of 8 atomic percent and a microstructure apparently unchanged from that before heating (Table III and Fig. 9). This sample had small, but definite, changes in its ultrasonic properties (Fig. 2 and Table II). Two succeeding heatings increased the hydrogen content to a total value of 14 atomic percent, which was still in Hägg's pure α-phase region. The ultrasonic properties of the sample changed a little more in the same direction. Another sample, Ti507, heated only once, behaved like Ti506 during the first heating (Fig. 3 and Table II).

These facts seem to lead to the interesting conclusion that the dissolved hydrogen decreases the attenuation of titanium slightly, while the velocity in the same material increases slightly. These changes are in the same direction as those induced by the appearance of the β-phase, although their magnitudes may differ considerably. Data on Ti514, Ti513, and Ti512 (Fig. 4 and Table II)supplied other evidence in this respect. Fig. 4 indicates that there is an intermediate set of attenuation values in between two extreme sets while Table II shows that there is an intermediate velocity value.

Craighead, Lenning, and Jaffee recently reported[4] that when the hydrogen content is below 33 atomic percent, all of the hydrogen is not in solution. By starting with vacuum annealed samples, they concluded, from the appearance of line marks in the microstructure, that a second phase appeared at room temperature when as little as 0.3 atomic percent of hydrogen was absorbed by titanium at 700°C. This precipitated second phase was identified as TiH. According to these findings, it then can not be concluded in the present study that all changes in ultrasonic properties through introduction of less than 33 atomic percent of hydrogen were effected by the presence of interstitial hydrogen atoms. It may be pointed out, on the other hand, that in the above mentioned report on line marks, it was not definitely established that all the absorbed hydrogen precipitated in the form of TiH at room temperature.

It is very tempting to infer that changes in ultrasonic properties, in the case of hydrogen content less than 33 atomic percent, had the same cause as those when the hydrogen content was over 33 atomic percent. This inference has its difficulties. For example, for some undetermined reason, although line marks were observed in some samples, they were not seen in Ti506 and Ti507. It has, moreover, not been proved that the phase characterized by the line marks discussed by Craighead, Lenning, and Jaffee is the same as the β-phase discovered by Hägg. In fact, there is very little reason to expect this to be the case. Experimental evidence, which will be presented in the following paragraph, further strengthens the belief that these two phases are different. If so, it has to be assumed that both phases tend to decrease the attenuation values while increase the velocity values.

When the results for Ti508 are compared with those for Ti506, it will be noticed that while the difference in amounts of hydrogen charged into the two samples was large, the difference in temperatures at which they were heated in hydrogen was small. When Ti506 was heated in hydrogen at 500°C. for 77 hours, its weight increased by 0.2%. On the other hand, the weight of Ti508 increased by 1.7% when the sample was heated for only 44 hours, but at 550°C. Ti508 was not the only sample which gained an extraordinary amount of weight on being heated at 550°C. During the second heating of the sample Ti508, Ti512, cut from a different titanium rod, was left in the furnace with Ti508, and the two were heated together for 61 hours. Although the weights of Ti512 were not measured, the gain in thickness (1.8%), the ultrasonic properties (Fig. 4 & Table II), and the microstructures after the heating (Fig. 10) indicated that it also took up a very large amount of hydrogen during heating. During this same heating, Ti508 gained another 1.0% in weight while with Ti507, in a second and third heating at 460°C. for 51 hours and at 500°C. for 65 hours respectively, the gains in weight were only 0.09% and 0.07% respectively. All of these facts point to the conclusion that between 500°C. and 550°C., the rate of absorption of hydrogen either rises more rapidly but continuously with temperature than at lower temperatures or that it has an abrupt increase as soon as a new phase appears at some temperature within the range under discussion. The latter mechanism seems more probable.

On returning to Ti508 itself, it will be noticed that after the sample was heated in vacuum twice, the apparent value of hydrogen content was reduced to only 9 atomic percent. The velocity of ultrasound had the same value as it did before the sample was heated in hydrogen at all (Table II). The attenuation, although recovering to some extent, was still far lower than before any heating in hydrogen. This suggests that the change in the structure of a sample due to the precipitation of a new titanium-hydrogen phase has much effect on the attenuation of the sample. It seems wrong to assume that replacing one phase by a second phase will cause a raising or lowering of attenuation solely in proportion to the fraction of the new phase present, and it seems certain that the manner of distribution of the new phase is very important. In contrast to attenuation, velocity of ultrasound is known to be insensitive to the change in structure.

One point of view given by Smith[8] in connection with the structure may be mentioned. It was pointed out that when titanium is charged with hydrogen, the lattice constants of the titanium change by rather large amounts. Either during the occlusion or the subsequent evolution of the gas, whenever there is a phase change, the phase boundary steadily migrates in the metal. This boundary cuts through the individual grains; consequently, a severe strain inside individual grains may be expected to accompany the arrival of the phase boundary. Smith maintained that the strain along the phase boundary introduces "rifts" or openings, even when a sample is kept at a room temperature. Ti508 was heated at about 550°C. during charging or removing of hydrogen. Whether this heating was sufficient to start some recrystallization is not known.

The concept of formation of rifts by the strain along the phase boundary may also offer an explanation for the mechanism discussed earlier, namely, that the rate of occlusion of hydrogen by titanium increases abruptly as a new phase appears. The surface of the matter at first gets enough hydrogen to form a new phase, the introduction of which allows a more rapid diffusion of hydrogen into the part adjacent to the phase boundary, because of the presence of rifts in the region already filled with the new phase.

The observed changes in the velocity of ultrasound can be attributed primarily to the changes in the density of the metal. According to the theory of elasticity, the velocity of propagation v of a longitudinal plane wave in an isotropic solid is given by the equation

$$v = \left(\frac{\lambda+2\mu}{\rho}\right)^{\frac{1}{2}}$$

where λ is Lamé's constant, μ the shear modulus and ρ the density of the solid. On assuming this equation to be valid in the present case, it is easy to see that if $\lambda+2\mu$ of titanium during charging or removing of hydrogen remained constant, then

$$\frac{v_1}{v_2} = \left(\frac{\rho_2}{\rho_1}\right)^{\frac{1}{2}}$$

where v_1 is the velocity when the density of a titanium-hydrogen system is ρ_1 and v_2 the velocity when the density is ρ_2. In Table V are listed the values of $\frac{v_1}{v_2}$ and $\left(\frac{\rho_2}{\rho_1}\right)^{\frac{1}{2}}$ at various stages of heating, the values all being compared with the velocity and the density of untreated titanium. It will be noticed that the values of $\frac{v_1}{v_2}$ are all very slightly larger than values of $\left(\frac{\rho_2}{\rho_1}\right)^{\frac{1}{2}}$ at the same stage. It means, therefore, $\lambda+2\mu$ also changed slightly with the hydrogen content. This is to be expected.

The data on attenuation can be arranged other than as given in Fig. 1 through Fig. 7. Instead of the maximum strain amplitude, a quantity related more closely to the internal friction may be presented as a function of frequency. Let

$$u(x) = u_o e^{-\alpha x}$$

for a plane wave travelling in the x direction, u(x) being the displacement at point x, then

$$I(x) = I_o e^{-2\alpha x}$$

where I(x) is the intensity at the same point. At the point $x+\lambda$ where $\lambda = \frac{v}{f}$, the displacement just repeats the value at an arbitrary starting point from which $\frac{v}{f}$ is measured,

$$I\left(\frac{v}{f}\right) = I_o e^{-2\alpha\frac{v}{f}}$$

v being, as before, the velocity of propagation and f the frequency. The quantity

$$\frac{I_o - I\left(\frac{v}{f}\right)}{I_o} = 1 - e^{-2\alpha\frac{v}{f}}$$

$$= 2\alpha\frac{v}{f} + \ldots\ldots\ldots \qquad \text{when} \quad 2\alpha\frac{v}{f} < 1$$

gives some measure of the fraction of energy dissipated during one oscillation. α is the attenuation value shown in Fig. 1 through Fig. 7 where it is measured in db/inch. It can be expressed in neper/centimeter by the use of the equation

$$\alpha(\text{db/in}) = 3.421\alpha(\text{neper/cm})$$

For Ti508 and Ti512, this quantity is shown in Figs. 13 and 14 as a function of frequency.

Ti513 was heated intermittently, first in Furnace A and then in Furnace B, these two furnaces having been described above in the section on experimental arrangements. The thickness and the ultrasonic attenuation of the sample and the velocity of ultrasound in the sample (Table II) were found to remain unchanged when the sample was heated in Furnace B for many hours. A few other samples heated in

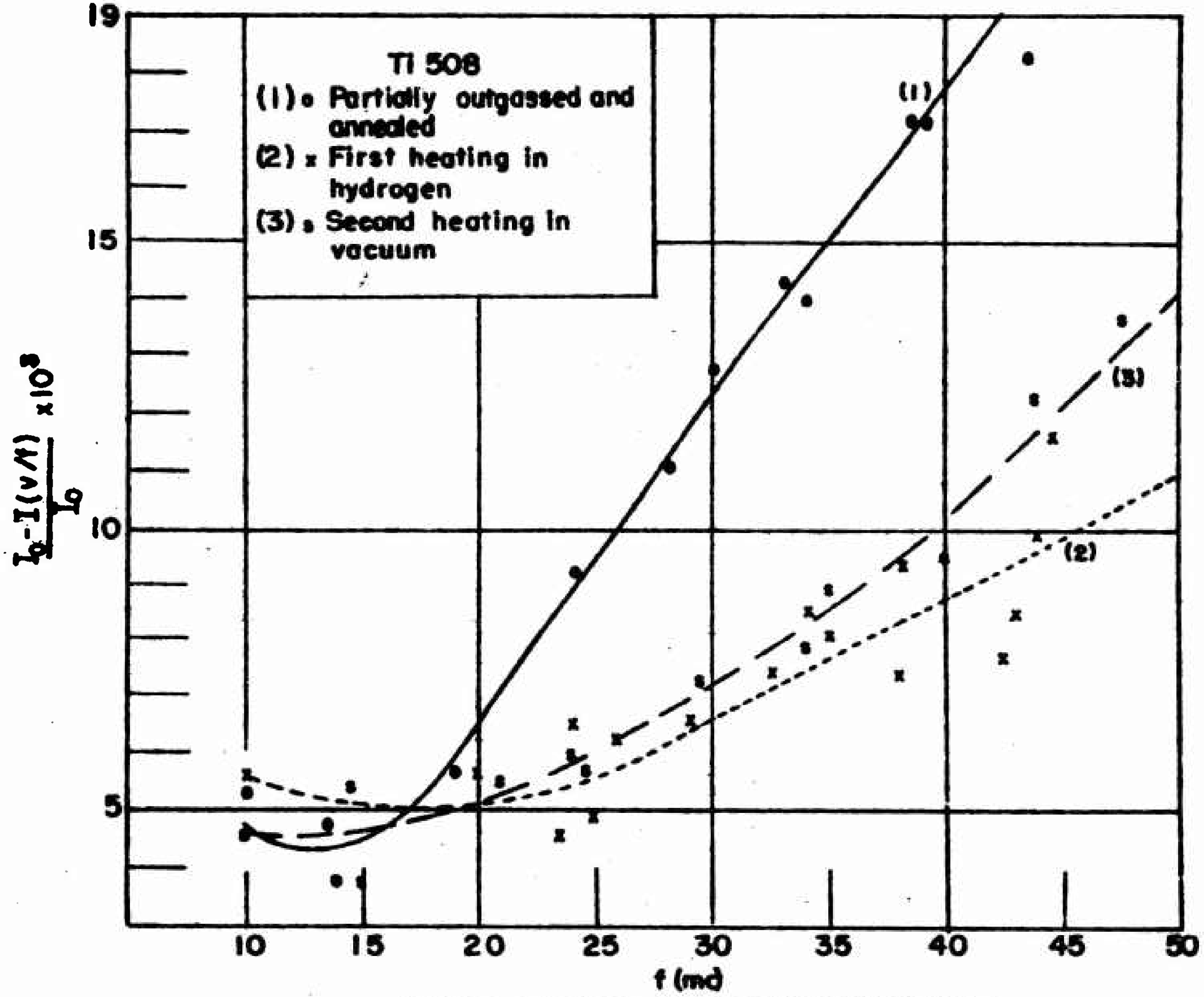


FIG. 13. ENERGY LOSS-FREQUENCY PLOT FOR Ti 508

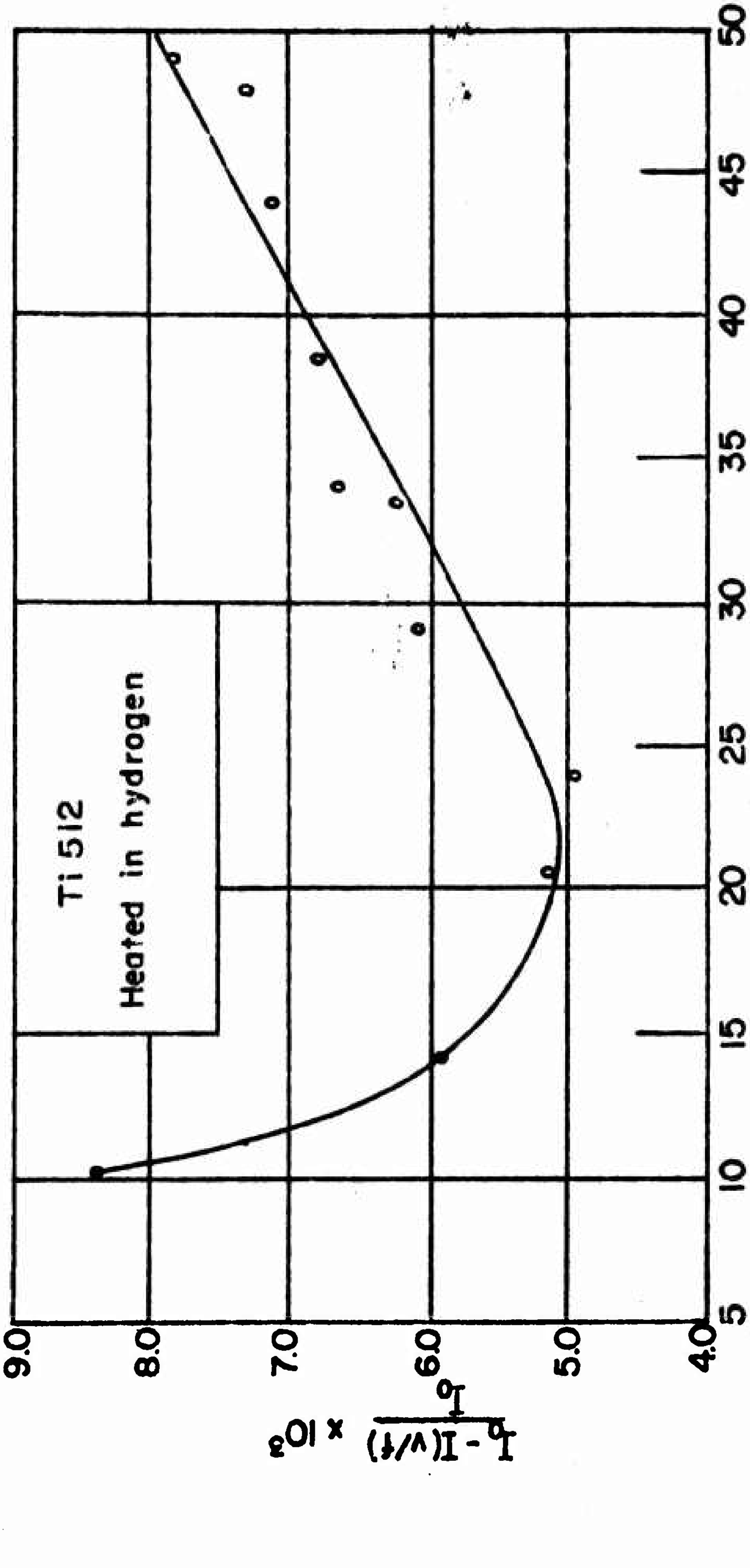


FIG. 14. ENERGY LOSS—FREQUENCY PLOT FOR Ti 512

Furnace B were also found to undergo no notable change in their thicknesses. As was mentioned earlier, while samples heated in Furnace A appeared grayish, samples heated in Furnace B had bluish, purple, or golden appearance. Although the same kind of commercial hydrogen was used for both furnaces, the atmosphere in Furnace B was almost certainly less pure than that in Furnace A because the former furnace is not as gas tight as the latter. Furthermore, one outlet of Furnace B was sealed with cold oil to facilitate quenching. It seems that some gas or vapor mixed in the hydrogen in Furnace B reacted with the surfaces of titanium samples and thereby retarded the penetration of hydrogen. In Fig. 10 are shown the microstructures of both the surface and the cross-section of Ti513, heated briefly in Furnace B after being heated several times in Furnace A. These two microstructures are different. Oxide or nitride on the surface of titanium was reported[7] to possibly inhibit hydrogen sorption at relatively low temperatures. This difference in the results of heating samples in Furnaces A and B is under further study. For example, oil has been taken away from Furnace B.

In heating samples intermittently, it has been intended to follow the change of microstructure, the ultrasonic attenuation, and the velocity of ultrasound while hydrogen diffuses into the samples. In particular, it has been intended to follow the penetration of the precipitated phase into the interior of a sample by examining the cross-section of the sample. The process by which the surface structure changes is also regarded as interesting. One preliminary result is given in Fig. 15 which shows the surface structure of T1513 after it was heated in Furnace A at 550°C. for a total of 17 hours. Curved lines were seen on the surface even without its being etched. It is not considered to be likely that these lines were the product of heat etching. Study along these lines is in progress.

VI. CONCLUSIONS

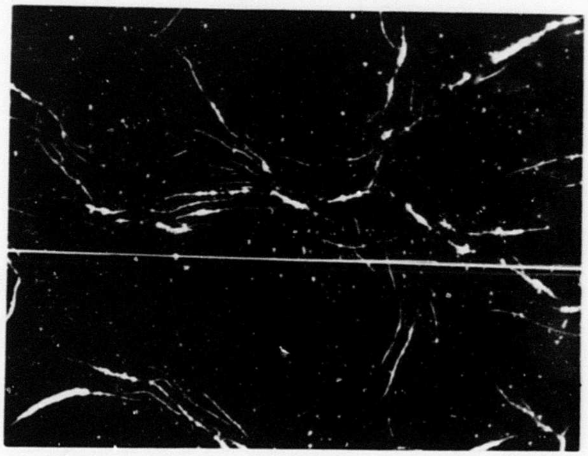
It is concluded that

(1) Commercially pure titanium, as received, has measurable attenuation values for longitudinal waves in the frequency range from 10 to 50 mc.

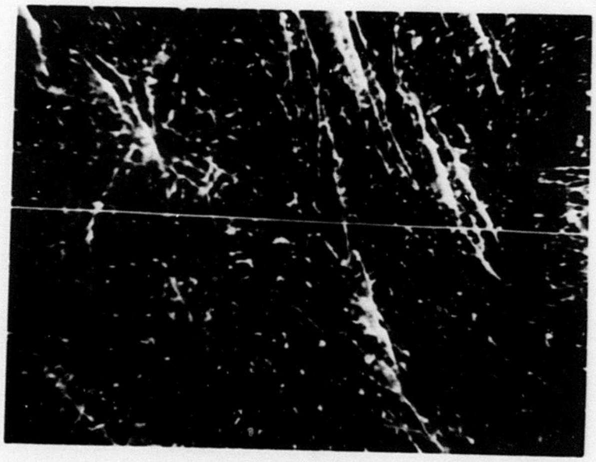
(2) The group velocity of ultrasound is around 5.85×10^5 cm/sec.

(3) On its being heated for many hours in vacuum, oxygen, or nitrogen at temperatures in the neighborhood of 600°C, the attenuation of, and the velocity in, titanium (commercially pure titanium) showed little change.

(4) When titanium was heated for many hours in hydrogen at temperatures ranging from 450°C to 550°C, the attenuation decreased while the velocity increased. Samples heated at high temperatures underwent remarkably large changes. In the case of velocity, values up to 6.52×10^5 cm/sec were



(a) Surface not etched



(b) Surface etched

Fig. 15
Photomicrographs of Ti513, heated in hydrogen at 550°C for 17 hrs. (The straight lines across the photographs are accidental scratches on the negatives of the photographs)

observed. In the case of attenuations, values changed up to 70% or more.

(5) In the same experiments as in (4), titanium samples increased in weight and volume, while decreased in density. Again, remarkably large changes of these quantities occured to samples heated to temperatures close to 550°C. Density changes as large as 11% were observed.

(6) From the relations between velocity and density, it can be deduced that some elastic constants of these samples also changed by small amounts through being heated in hydrogen.

(7) Very long lines or needles replaced or covered the regular grains of samples heated in hydrogen at temperatures close to 550°C. Samples heated below 500°C did not show very noticeable changes in their microstructures.

(8) On being heated in vacuum for many hours at 550°C, a sample which had been heated for many hours in hydrogen at 550°C before, lost much weight and volume. Its density, and the velocity of ultrasound in it, finally restored their values they had before any heating. Its ultrasonic attenuation was higher than before vacuum heating but still lower than before any heating.

(9) Comparison between data on a sample heated at 550°C in hydrogen and those heated at 500°C suggests that there is a rapid, or possibly abrupt, increase in the rate of absorption of hydrogen by titanium at temperatures between 500°C and 550°C.

(10) The changes in velocity in treated titanium through various treatments can be attributed, for the major part, to the changes in density.

(11) In the case that a sample absorbed such a large amount of hydrogen that it had a microstructure of very long lines or needles, the large changes in attenuation are believed to be caused by the appearance of a new titanium-hydrogen phase, very likely Hägg's β-phase.

(12) In the case that the hydrogen content of a sample was small and its microstructure regular, the cause of a small decrease in attenuation is not well understood. Because of the recent discovery[4] that titanium hydride is formed even when the hydrogen content in the titanium is very small, it is not known whether hydrogen in solution or hydrogen in the precipitated form or both are responsible for the small decrease in attenuation. One fact, which probably should not be over-looked, is that at small hydrogen content, the portion of the hydrogen in solution relative to the portion in precipitates is larger than at large hydrogen content.

(13) Certain impurities in the hydrogen are believed to be able to so react with the surface of titanium that the penetration of hydrogen into the metal is retarded.

(14) Interesting information about diffusion may be obtained by following the change in the microstructures of both the surface and the cross-section, as well as in the ultrasonic properties, of titanium, as heating in hydrogen progresses. Further investigation along this line is underway.

Bibliography

1. L. Kirschfeld and A. Sieverts: Z. physik. Chem. A 145, 227 (1929).
2. G. Hägg: Z. physik. Chem. B 11, 433 (1931).
3. P. Ehrlich: Ztsch. anorg. allgem. Chem. 247, 53 (1941).
4. C. M. Craighead, G. A. Lenning, and R. I. Jaffee: Trans. AIME 194, 1317 (1952); J. Metals (Dec. 1952).
5. R. L. Roderick and R. Truell: J. Appl. Phys. 23, 267(1952).
6. W. P. Mason and H. J. McSkimin: J. Appl. Phys. 19, 940 (1948)
7. C. F. P. Bevington, S. L. Martin, and D. H. Mathews: Proc. Intern. Congr. Pure and Applied Chem. (Lond.) 11, 3 (1947).
8. D. P. Smith: Hydrogen in Metals, University of Chicago Press, Chicago, Ill. (1947).