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Part 1

HYDROGEN CONTAMINATION IN TITANIUM AND TITANIUM ALLOYS

Part 1. Hydrogen Embrittlement in Alpha-Beta Titanium Alloys

(Report of WADC Technical Meeting 29 October 1954)

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FOREWORD

This report was prepared by the Metals Branch and was initiated under Project No. 7351, "Metallic Materials," Task No. 73510, "Titanium Metal and Alloys," and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Lt Harris M. Burte acting as project engineer.

This report contains papers presented at a Wright Air Development Center technical meeting 29 October 1954.

ABSTRACT

Hydrogen contamination in alpha-beta titanium alloys can cause low ductility in slow strain rate, room temperature tensile tests, and premature brittle fracture in room temperature rupture tests. The combination of stress concentrations and hydrogen contamination can lead to a drastic decrease in the load carrying capacity of these alloys. Another result of hydrogen contamination is increased susceptibility to embrittlement as a result of exposure to stress and elevated temperature.

At the present time, a maximum hydrogen content of 125 parts per million is suggested as a tolerance for aircraft quality alpha-beta titanium forging alloys. Data are presented which show that in the future it will be possible to produce alloys which have much higher tolerances for hydrogen.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES (cont'd)

LIST OF ILLUSTRATIONS

Figure | Page

Hydrogen Embrittlement of Alpha-Beta Titanium Alloys

LIST OF ILLUSTRATIONS (cont'd)

LIST OF ILLUSTRATIONS (cont'd)

Shear Cracking of Commercial Ti-8% Mn Sheet

LIST OF ILLUSTRATIONS (cont'd)

Figure | Page

The Effects of Hydrogen on The Mechanical Properties of Titanium

LIST OF ILLUSTRATIONS (cont'd)

INTRODUCTION

In July 1954 the Materials Laboratory, Directorate of Research, Wright Air Development Center initiated an intensive research program into the effects of hydrogen contamination in titanium and titanium alloys. A lack of information on this subject had threatened to hinder Air Force application of titanium alloys. The first results of the program were presented at a technical meeting held at WADC on 29 October 1954; this report contains the papers and discussions presented at this meeting.

SUMMARY AND CONCLUSIONS

The effects of hydrogen on the properties of alpha-beta titanium alloys are different than the effects on all alpha alloys. At present, most of the commercially available alloys are of the alpha-beta type, and this summary of the papers pertains to these alpha-beta alloys.

1. Hydrogen contamination in the titanium alloys being used by airframe and jet engine manufacturers during the summer of 1954 ranged from 50 parts per million to over 400 parts per million. (It should be mentioned that, due to recent modifications in melting procedure by some of the titanium vendors, current production titanium may have less hydrogen than much of the material which was analyzed.)

2. Hydrogen contamination in alpha-beta alloys can cause low ductility as measured in a room temperature, slow strain rate tensile test. It has little effect on properties measured in fast rate tensile tests.

3. Hydrogen contamination in alpha-beta alloys can cause premature brittle fracture in room temperature rupture tests. <u>The combination of stress concentrations and hydrogen contamination can lead to a drastic decrease in the load carrying capacity of the material</u>.

4. This embrittlement by hydrogen is time dependent, and may become evident only after the material has been stressed for many hours.

5. The hydrogen level at which these characteristic effects on room temperature properties becomes evident probably depends upon chemical composition (both major alloying elements and contamination by oxygen, nitrogen and carbon), and upon microstructure or heat treatment.

6. These characteristic effects of hydrogen on the room temperature properties of alpha-beta alloys disappear when testing is conducted at elevated temperatures, and may be accentuated at reduced temperatures. At elevated temperatures, however, hydrogen contamination can cause a different type of embrittlement.

7. Hydrogen contaminated alpha-beta alloys which are exposed to stress and elevated temperatures may be brittle in subsequent room temperature, fast rate tensile tests.

8. No correlation has been found between hydrogen contamination and shear cracking in alloy sheet.

9. Until the effects of the many possible factors contributing to hydrogen embrittlement can be evaluated and brought under control, <u>a maximum hydrogen content of 125 parts per million is suggested as a tolerance for aircraft quality alpha-beta titanium forging alloys.</u> It is not too severe a requirement, and in some cases may even be too high.

10. Several different methods are in use for chemical analysis of hydrogen. Over 20 laboratories are now engaged in a round-robin program to evaluate these methods.

11. Two of the materials which were tested were not embrittled by hydrogen contents over 250 parts per million. Therefore, by suitable control of composition and/or heat treatment, it should be possible to produce alpha-beta titanium alloys which have high tolerances for hydrogen.

WORDS OF WELCOME

by

Colonel J. V. Hearn, Jr.

Gentlemen: The Materials Laboratory is pleased to be the host of this very important technical meeting. I speak for the Center Commander, Major General Boyd, as well as the Materials Laboratory when I welcome you to Wright Air Development Center.

As you all know, the development of titanium from a Laboratory curiosity to a useful metallic aircraft material has been more rapid than for any other metal. As in the case of all new materials, many development difficulties have had to be overcome. It is essential to the timely solution of these basic problems that we have free exchanges of technical data and research experiences. This then is the objective of our meeting: To give you, the producers and consumers, the benefit of our experiences in a specific problem area.

Major Kotfila will give you the details of the Hydrogen Embrittlement in Titanium Program. I will not take your valuable time to dwell on the importance of the problem -- your presence here is evidence that it is well appreciated. I hope you will find the discussions interesting and informative.

Some of you are frequent visitors to the Materials Laboratory. Others may not be familiar with our facilities or activities. We invite you to come in and get acquainted at your earliest opportunity. Whether your problems be in titanium or in other aircraft materials, we hope you will make them known.

ROLE OF INTERSTITIALS IN TITANIUM AND TITANIUM ALLOYS

by

Major R. J. Kotfila

The role of interstitials in titanium has been, is now, and will be the subject of many investigations. Many papers have been written describing the effects of O_2, N_2, C, and H_2 on the properties of titanium. At one time these interstitials were used as alloying additions; today, these same interstitials have fallen into the greatest depths of disrepute. Whenever titanium failed during fabrication or showed erratic behavior, the interstitials, collectively and/or individually, were blamed. In most instances, little or no data were presented to substantiate this conclusion. As a result, the overall relation of the effect of interstitials to the problems existing today is not clear.

Commercial production of titanium dates back less than ten years. In these ten years, this metal has been pressed into service at a pace unprecedented in metallurgical history. Concurrent with this phase, extensive research has been conducted, a portion of which was concentrated on the effects of interstitials. The alpha stabilizing interstitials O_2, N_2, and C received the most attention since titanium has a great affinity for these elements and since the problem of hydrogen pickup during processing was not considered serious.

The following is a brief summary on the effect of the alpha stabilizing interstitials: Added to pure titanium, they strengthen the metal but reduce its ductility and impact strength. Welds in titanium can be seriously embrittled by their presence in the parent metal or by pickup from the welding atmosphere. Carbon, present as titanium carbides in any large amount, not only impairs machineability but also embrittles the metal. The effects of these interstitials appear to be additive, therefore it is not only the individual content of the element that will determine the degree of embrittlement but the total interstitial content.

The interstitial tolerance of the alpha-beta type alloys will vary with the composition of the alloy. The effect on alloys is essentially the same as it is on pure titanium; there is a strengthening effect associated with a decrease in ductility and loss in impact strength. The beta phase of the alpha-beta type alloys is especially intolerant to interstitials and consequently the alpha-beta ratio will be one of the governing factors in any determination of the detrimental effect of these interstitials. It has been postulated that the alpha phase will act as a getter for oxygen, carbon and nitrogen leaving the beta phase soft and ductile. If this hypothesis is correct, the importance of alpha-beta ratio cannot be overemphasized.

Today, as in the past, titanium alloys have been used in the annealed condition. In the future, the design engineers will intend to exploit the full potentialities of these alloys; this will require heat treatment to obtain high strength levels. Frost, Parris and their coworkers at Battelle and Luini and Hanink of Curtiss-Wright have shown that by quenching and aging, strengths up to 180,000 - 200,000 psi are possible with the alloys in existance today. The interstitial effect will be more pronounced at these high strength levels. Further, the interstitial content will undoubtedly govern to some extent the heat treat response of these alloys. Hansen and Rostoker of Armour have already reported that oxygen in titanium alloys accelerates the transformation process and that the knee of the TTT curves is shifted to the left with increasing O_2 content. Research on the heat treat response of commercial alloys with varying interstitial content is now underway.

The strengthening effect of interstitials diminishes, if it does not completely disappear, at the elevated temperatures. McPherson and coworkers at Armour have observed that no difference in stress-rupture life at 550°C was obtained from iodide base alloys and alloys made from 140 BHN sponge. However, the iodide base alloys did tend to show greater elongations and higher minimum creep rates.

These are the more salient effects of the alpha stabilizing interstitials. This summary is by no means complete as further research in this area is in progress.

Data on the effects of <u>hydrogen</u> are rather limited. This element has a high solubility in beta and is considered a <u>beta stabilizing interstitial</u>. Hydrogen is introduced into titanium by one or more of the following methods.

1. Pickup occuring during the production of sponge
2. Acid leaching of sponge
3. Hygroscopic action of $Mg\ Cl_2$ salts during storage of sponge
4. Pickling in acid solutions
5. Descaling in sodium hydride salts.

A literature search on the effects of hydrogen on titanium and titanium alloys will show that the work of Craighead, Lenning and Jaffee is the most comprehensive in this field.

The following is a summary of their early work on high purity titanium, commercial purity titanium, and alpha titanium alloys. The effect of H_2 on the mechanical properties is to decrease notch toughness without affecting tensile properties. The cause for this effect appears to be an increased sensitivity to notches. Impact strength is drastically reduced by even small additions of this element. Jaffee and his coworkers have also shown that the effects of hydrogen on alpha-beta titanium alloys are different than the effects on alpha alloys. They suggested hydrogen tolerances for two alpha-beta alloys on the basis of loss of ductility in a slow rate tensile test. The 8% manganese alloy suffers a precipitous loss in reduction of area at about 1 atomic percent H_2; the tensile ductility of the 4% Mn-4% Al alloy was not appreciably affected by hydrogen additions up to 4.4 atomic percent.

Unlike the alpha stabilizing interstitials, hydrogen can be removed from titanium by vacuum annealing. It is unlike steel where hydrogen can be removed by heating or baking at moderately elevated temperatures in an air atmosphere.

This Center first became aware of the magnitude and scope of the hydrogen problem in the early days of this year. A 200 lb. ingot of an alpha-beta alloy, the 3% Mn complex alloy, was melted by the Bureau of Mines and was given to a commercial titanium producer for processing into bar stock. The finished bars were to be released to aircraft companies for evaluation. In a preliminary evaluation by the commercial producer and a research laboratory, a serious difference in properties was found to exist, especially in tensile ductility. In a conference held to establish the cause for this disagreement, it was determined that strain rate after passing the yield point was different in the two tests, and that this may have been the reason for the difference in properties. In a series of tests conducted at the Materials Laboratory, results of the two previous series of tests were duplicated by simply varying the strain rate. The hydrogen content of the bars as determined by vacuum fusion analysis was 200 ppm. At that time, it was recommended that wherever possible, a duplicate check on tensile ductility be made using a slow rate tensile to determine if any hydrogen contamination does exist in the material under test. A more complete investigation of this phenomenon was made and the results have already been published.

Shortly after this investigation was completed, an aircraft gas turbine manufacturer reported a series of failures which were attributed to hydrogen embrittlement of the alpha-beta alloy being used. This was corroborated by analysis and a series of tests on vacuum annealed material. The personnel at this company adopted a notch stress rupture test at room temperature to determine the degree of hydrogen embrittlement of material in their shop.

Their inventory represented many heats, and the results of stress-rupture testing indicated that all heats were seriously contaminated with hydrogen. At this point, the application of titanium on jet engines at that plant was halted, an action which seriously disrupted the Air Force procurement schedule and in general, caused some uneasiness in the titanium industry. To forestall further possible setbacks in procurement and to remove the aura of mystery surrounding this problem, the Materials Laboratory, of this Center, began an extensive investigation of the hydrogen embrittlement phenomenon. The first and most immediate task was to determine the hydrogen tolerances of the more popular commercial alloys. The second task was to sample material on hand in aircraft and engine plants to determine the degree of hydrogen contamination. As a stopgap measure, Air Force Specification Bulletin 108 was issued which, among other quality requirements, limited the hydrogen content of all wrought titanium alloy products, excluding sheet, to 125 ppm.

The program as outlined originally was ambitious. However, after approximately four months of work, it was felt that enough information has been gathered to issue a progress report. The papers to be presented today constitute this progress report.

HYDROGEN EMBRITTLEMENT

OF ALPHA-BETA TITANIUM ALLOYS

by

Lt Harris M. Burte

Introduction

The first part of this paper is a discussion of the effects of hydrogen contamination on the mechanical properties of alpha-beta titanium alloys. (Alpha-beta alloys are those in which both the hexagonal close packed phase alpha, and the body centered cubic phase beta coexist at room temperature) A simple mechanism of hydrogen embrittlement is proposed. Illustrative data are presented for cylindrical specimens from bar stock. A discussion of flat specimens from sheet is contained in a later paper(1).

The second part of the paper presents some of the data obtained in an attempt to determine the hydrogen tolerances of several alpha-beta titanium alloys available as bar-stock. Data for alloys available as sheet are presented in a later paper(1).

Experimental Methods

The materials discussed in this paper are described in Tables 1 and 2. More complete chemical analyses are being obtained. The preparatory procedures described in Table 3 were performed on the as-received stock in order to obtain different levels of hydrogen contamination in specimens from one heat of a given material. In most cases, the materials of different hydrogen levels prepared from one heat were brought to similar thermal histories before test specimens were machined. Thus, vacuum annealed (low hydrogen) material is usually compared with as-received or hydrogenated material which has been given thermal treatments in air or an inert gas equivalent to the thermal treatment involved in vacuum annealing. The thermal treatments in air or inert gas did not affect the hydrogen level.

Details of mechanical property test procedures are presented in the next paper(2). Notched specimens had a circumferential V-notch with a theoretical stress concentration factor ~ 2.7. Tensile tests were performed at two rates; for unnotched specimens which broke in a ductile manner the fast rate required approximately 2 minutes to fracture; the slow rate required approximately 10 minutes.

The photomicrographs are representative of material which has not been deformed in a mechanical property test. They are taken perpendicular to the long axis of the bar stock. The magnification is 500X. Metallographic specimens were mechanically polished, and were etched with one of the following mixtures:

48% HF	= 2% (by volume)	2%	20%
conc. HNO_3	= 10%	-	20%
H_2O	= 88%	98%	-
glycerine	= -	-	60%

Hydrogen analyses were by the vacuum fusion method.

The Effects of Hydrogen Contamination on The Mechanical Properties of Alpha-Beta Titanium Alloys

Tensile properties. Tensile test data obtained on specimens from one heat of titanium alloy Ti-140A are presented in Figures 1 and 2. Over the range investigated, hydrogen contamination has little effect on the unnotched or notched tensile strengths measured at either the fast or slow testing speeds. Similarly, hydrogen contamination has little effect on the elongations or reductions in area measured at 200°F or higher. At room temperature and -70°F hydrogen content does not affect the elongation or reduction in area measured at the fast strain rate. However, elongation and reduction in area for the high hydrogen content material (250 parts per million) are much less when measured at the slow strain rate than when measured at the fast strain rate.

Rupture properties. The rate of deformation of a specimen in a rupture (sustained loading) test can be much less than the rates at which it is practical to deform a material in a tensile test. Table 4 shows the results of room temperature rupture tests on unnotched specimens of hydrogenated titanium alloy RC-130B. The effect of rate of deformation is clear; at the lower stresses, andtherefore slower rates of deformation, the reductions in area become quite small.

Table 5 presents some results of room temperature rupture tests on unnotched specimens of the titanium alloy Ti-140A for which tensile data were given above (A ">" (greater than) symbol before a time value indicates that the specimen did not fracture, and that the test was discontinued.) Two conclusions are evident:

a. The hydrogen containing specimens fractured in a brittle manner.

b. The hydrogen containing specimens fracture after relatively short times at stress levels where the low hydrogen materials did not fracture in very long times. Note that contrary to the results of the slow tensile tests at room temperature (Figure 1), the rupture tests indicate that the material containing 170 parts per million (ppm) hydrogen is susceptible to embrittlement. This is another illustration of the strain rate dependence of the ductility of hydrogen contaminated alpha-beta alloys. It is presumed that this 170 ppm material would show evidence of embrittlement in the tensile test if a very much slower rate were used, but as a practical matter it is easier to perform the rupture test.

The results of room temperature rupture tests on notched specimens of the titanium alloy Ti-140A are shown in Figure 3. (Points with an arrow leading to the right indicate that the specimen did not fracture.) Hydrogen contamination of 170 ppm is sufficient to cause premature fracture. Note that the notched specimen of the material containing 250 ppm hydrogen stressed at 98,000 psi fractured in 4 hours, whereas an unnotched specimen of the same material stressed at 101,000 psi did not fracture in 1244 hours (Table5).

The results of room temperature tensile and rupture tests on notched specimens of the titanium alloy RC-130B are shown in Figure 4. (The height of the vertical line rising from a point is proportional to the reduction in area at fracture.) These results supplement those discussed above: the hydrogen contaminated specimens fracture in relatively short times at stresses where the low hydrogen specimens do not fracture; at the lower stresses, and therefore lower rates of deformation, the hydrogen contaminated specimens fracture in a brittle manner.

The results of some elevated temperature rupture tests on specimens of the titanium alloy Ti-140A are presented in Tables 6 and 7. At the elevated temperatures there were no examples of premature brittle fracture. Thus, the characteristic effects of hydrogen contamination that are measured at room temperature, low ductility in slow tensile tests and premature brittle fracture in rupture tests, disappear when testing is conducted at elevated temperatures. In a later paper[3], however, Wruck will show that hydrogen can cause an embrittling reaction at these elevated temperatures. Hydrogen contaminated specimens of Ti-140A which have been exposed to stress and elevated temperatures are shown to be brittle in subsequent room temperature fast rate tensile tests.

<u>General</u> - These effects of hydrogen contamination on room temperature mechanical properties, namely the strain rate dependence of ductility measured in tensile tests, and premature brittle fracture in rupture tests, should be applicable to all alpha-beta titanium alloys. To date, they have been observed in alloys with the following nominal compositions:

Ti-1.5Fe-2.7Cr
Ti-2Fe-2Cr-2Mo
Ti-3Mn-1Fe-1V-1Cr-1Mo
Ti-8Mn
Ti-4Al-4Mn

The hydrogen level at which these embrittlement effects first become noticeable will probably depend upon:

a. Composition (major alloying additions),
b. Level of contamination by the other interstitials (oxygen, nitrogen, and carbon)
c. Prior thermal history (heat treatment).

A review of hydrogen embrittlement in steels has been prepared by Sachs and Beck[7]. It is interesting to note that the effects of hydrogen on the mechanical properties of alpha-beta titanium alloys are very similar to the effects of hydrogen on the mechanical properties of steel.

Discussion - For hydrogen contaminated material, the ductility measured in room temperature tensile tests depends upon the strain rate (Figure 1); at slow strain rates, low ductilities are obtained. The following mechanism of embrittlement is suggested. Initially, in the undeformed material, most of the hydrogen is probably in interstitial solid solution in the beta phase. It is assumed that in the deformed material there is a tendency for microsegregation of the hydrogen; one possible reaction involves precipitation of a hydride phase at dislocations, phase boundries, or other crystallographic flaws. Whatever the result of the microsegregation, it provides places where, under the influence of the applied stress, microcracks can be initiated and propagate thus causing premature brittle fracture.

Since it involves diffusion, the microsegregation of the hydrogen takes time. The ductility obtained in a tensile test will depend upon the relative rates at which the material is deformed, and at which the hydrogen diffuses. In the fast strain rate tensile test at room temperature the rate of deformation is greater than the rate of microsegregation of the hydrogen. Thus the material fractures in a ductile manner before there is enough microsegregation to cause embrittlement. Conversely, in the slow strain rate tensile test appreciable embrittlement occurs before there has been time for extensive deformation, and the material fractures in a relatively brittle manner.

The rate of diffusion of hydrogen should decrease as the temperature decreases. Thus, a strain rate which is sufficiently slow to allow embrittlement in a tensile test at one temperature may not be slow enough at much lower temperatures. The tendency towards embrittlement is not removed at these lower temperatures (as will be discussed below, it is probably increased); it merely takes a longer time for this tendency to become evident. Therefore, in tensile tests performed at a given strain rate on hydrogen contaminated material, it is possible for the reduction in area to go through a minimum as temperature is decreased. Results of this nature have been obtained by Erbin[5] and by Ripling[6].

Embrittlement by the mechanism suggested above should have pronounced effects on room temperature rupture tests. A small amount of deformation of the specimen is sufficient to promote microsegregation of the hydrogen with consequent formation and propagation of microcracks. Since at low stresses the rate of deformation can be made quite slow relative to the rate of embrittlement, the fractures may be very brittle (Table 4). Furthermore, the initiation and propagation of microcracks causes the specimen to fracture at low stress levels, where, for hydrogen free material not subject to this type of embrittlement, the rate of deformation is so slow that fracture would not occur in time periods of practical interest (Table 5).

The stress concentration in a notched rupture specimen causes deformation to occur at the root of the notch at nominal stresses much lower than those required for a slight amount of deformation in unnotched specimens. Thus the deformation needed to promote the microsegregation of hydrogen and consequent embrittlement will occur at lower nominal stresses in notched specimens than in unnotched specimens.

The net effect of hydrogen contamination on room temperature rupture tests will be premature brittle fracture.

The characteristic effects of hydrogen on room temperature properties, namely low ductility in slow tensile tests and premature brittle fracture in rupture tests, disappear when testing is conducted at 200°F or higher. In a later paper Jaffee(4) will suggest that the hydrogen level required for embrittlement decreases as the temperature is decreased. Therefore, it is possible that at the elevated test temperatures the solubility of hydrogen in the parent metal is increased so much that, at the hydrogen levels studied, there is no tendency towards microsegregation even in the deformed material. An alternate possibility is that microsegregation does take place at the elevated temperatures, but that the general level of ductility at these elevated temperatures is sufficiently high so that crack initiation and propagation does not occur. Since an embrittling reaction due to hydrogen can occur at the elevated temperatures(3) this second possibility should be considered. It is rendered unlikely by the fact that the ductility for low hydrogen material does not increase very much between room temperature and 600°F. It is quite possible, therefore, that the mechanism of this elevated temperature embrittlement is not the same as the microsegregation considered in this paper; alternate mechanisms will be proposed by Wruck(3).

Hydrogen Tolerances For Specific Alloys

Introduction - Experiments have been performed to obtain information on the levels of hydrogen contamination which will produce embrittlement in some of the alpha-beta titanium alloys now available. Room temperature tensile and rupture tests were performed. The materials tested are described in Tables 1, 2 and 3.

In general, one or more high hydrogen levels for a given heat are compared to a vacuum annealed, low hydrogen control lot which is presumed to be free of hydrogen embrittlement. To date, little work has been done at hydrogen levels between 50 and 150 ppm.

It must be emphasized that a high hydrogen tolerance for a given alloy can not be established on the basis of data from one heat, even if the data indicate that a certain hydrogen level does not cause embrittlement. Material from another heat with a slightly different chemistry, or indeed from the same heat with a different thermal history might show embrittlement at this hydrogen level.

Ti-140A, Ht. M1170. Many of the data for this material were used to illustrate the discussions in the first part of this paper. Three hydrogen levels 20, 170 and 250 ppm were investigated. Photomicrographs of the conditions that were tested are shown in Figures 5, 6 and 7. Some results of slow and fast rate room temperature tensile tests on unnotched specimens are presented in Figure 8. Some results of room temperature rupture tests on unnotched and notched specimens are presented in Tables 5 and 8 respectively. At a hydrogen level of 170 ppm the material is not brittle in the slow tensile tests, but premature brittle fractures do occur in the rupture tests. A hydrogen content of 250 ppm causes embrittlement in both the slow tensile and the rupture tests. The high reduction in area (9.4%) shown by one of the notched rupture samples of the high hydrogen material was probably due to experimental error. Reduction in area of a notched sample was difficult to measure, and the results occasionally showed bad scatter.

Ti-140A, Ht. M1192. The material at a hydrogen level of 210 ppm was tested in two heat treated states: furnace cooled from 1200°F, and air cooled from 1350°F. Photomicrographs of these conditions are shown in Figures 9 and 10. The results of room temperature rupture tests on notched specimens are presented in Table 9. There is evidence of embrittlement in the material furnace cooled from 1200°F. The absence of premature fracture in the specimens of the material air cooled from 1350°F, indicates that this heat treated state has a higher hydrogen tolerance than the state of furnace cooled from 1200°F. Air cooling from the higher temperature increases the ratio of beta phase to alpha phase.

Ti-150A, Ht. R68. Two hydrogen levels, 10 and 250 ppm were investigated. Photomicrographs of the conditions tested are shown in Figures 11 and 12. The results of slow and fast rate room temperature tensile tests on unnotched specimens are presented in Figure 13. The results of room temperature rupture tests on unnotched and notched specimens are presented in Tables 10 and 11 respectively. The high hydrogen material shows strain rate sensitivity in tensile tests, and a pronounced tendency towards premature brittle fracture in rupture tests. These results are characteristic of very severe hydrogen embrittlement.

Ti-150A, Ht. M308. The high hydrogen condition tested was the as-received state; it was not adjusted to a thermal history equivalent to the low hydrogen (vacuum annealed) state. The two hydrogen levels investigated were 30 and 160 ppm. The results of room temperature rupture tests on notched specimens are presented in Table 12. At the lower loads, specimens of the high hydrogen material fracture prematurely, in a brittle manner.

Ti-155 AX. The vendor's heat designation for this material was unknown. Two hydrogen levels, 5 and 260 ppm were investigated. Photomicrographs of the conditions tested are shown in Figures 16 and 17. The results of slow and fast rate room temperature tensile tests on unnotched specimens are presented in Figure 18. The results of room temperature rupture tests on unnotched and notched specimens are presented in Tables 13 and 14 respectively. None of the tests show any evidence of hydrogen embrittlement. Note the long time, yet ductile fracture shown by the unnotched rupture specimen of the high hydrogen material which was loaded at 156,000 psi.

RC-130B, Ht. B5038. Some of the data for this material were used to illustrate the discussions in the first part of this paper. Two hydrogen levels, 10 and 320 ppm were investigated. Photomicrographs of the conditions tested are shown in Figures 19 and 20. The results of slow and fast rate room temperature tensile tests on unnotched specimens are presented in Figure 21. Results of room temperature rupture tests on unnotched and notched specimens are presented in Table 15 and Figure 4 respectively. Although the material at 320 ppm hydrogen does not show embrittlement in the slow tensile test, it does show premature brittle fractures in the rupture tests.

RC-130B, Ht. B3371. Four hydrogen levels, 60, 150, 190 and 280 ppm were investigated. Photomicrographs of the conditions tested are shown in Figures 22, 23, 24 and 25. The results of some room temperature rupture tests on notched specimens are presented in Table 16. There is evidence of embrittlement at a hydrogen level of 150 ppm.

Ti-6Al-4V, Experimental heat. This alloy composition, at present in an experimental stage, is receiving much attention because of its attractive elevated temperature strength and stability. Two hydrogen levels, 5 and 270 ppm were investigated. Photomicrographs of the conditions tested are shown in Figures 26 and 27. The results of slow and fast room temperature tensile tests on unnotched specimens are presented in Figure 28. The results of room temperature rupture tests on unnotched and notched specimens are presented in Tables 17 and 18 respectively. None of these tests show any evidence of embrittlement due to hydrogen.

Discussion. The results of the tests on the alpha-beta titanium alloys are summarized in Table 19. No data were obtained at hydrogen levels between the ones shown in Table 19, and the low levels of the vacuum annealed control lots. For materials embrittled at the hydrogen level indicated, it is not know how closely the vacuum annealed level must be approached before ductile behavior is attained.

Since only one heat and one heat treated state each of the Ti-155AX and Ti-6Al-4V alloys were tested, there are not yet enough data to support high hydrogen tolerances for these alloy compositions.

On the basis of the data presented, and until the effects of the many possible factors contributing to hydrogen embrittlement can be evaluated and brought under control, a maximum hydrogen content of 125 ppm is suggested as a tolerance for aircraft quality alpha-beta titanium forging alloys. It is not too severe a requirement, and in some cases may even be too high.

Conclusions:

1. Low ductility in slow rate room temperature tensile tests, and premature brittle fracture in room temperature rupture tests are characteristic effects of hydrogen contamination in alpha-beta titanium alloys.

2. These characteristic effects disappear when testing is conducted at elevated temperatures, and may be accentuated at reduced temperatures. At elevated temperatures, however, hydrogen contamination can cause a different type of embrittlement.

3. A maximum hydrogen content of 125 ppm is not too severe a requirement for the alpha-beta titanium forging alloys now available.

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2. Klinger, R. F., and Rector, W. H., "Mechanical Property Test Methods Used For The Evaluation of Hydrogen Embrittlement", This report.

3. Wruck, D. A., "Creep Embrittlement of Titanium Alloys", This report.

4. Jaffee, R. I., "Effects of Hydrogen on The Mechanical Properties of Titanium", This report.

5. Erbin, E. F., "The Effects of Heat Treatment on The Hydrogen Embrittlement of a High Strength Titanium Alloy", This report.

6. Ripling, E. J., Private communication, work performed under Contract AF 33(616)-2223.

7. Sachs, G., and Beck, W., "Survey of Low-Alloy Aircraft Steels Heat Treated to High Strength Levels, Pt. 1 Hydrogen Embrittlement", WADC Technical Report 53-254, Part 1, December 1953.

DISCUSSION

Frazier: Can you give us an idea of the pressures used in vacuum annealing?

Burte: The pressure, measured in a room temperature zone in the system, was usually below 0.1 micron, and sometimes was as low as 0.01 micron, We, of course, were using research scale equipment. The vacuum annealing temperatures (Table 3) were chosen in order to obtain certain heat treated conditions, and are probably much lower than temperatures that would be used in a commercial vacuum anneal.

Johnson: Is embrittlement strictly a function of the beta phase? Is there no contribution from alpha phase, unless as a resevoir for hydrogen?

Burte: Dr. Jaffee has shown that hydrogen is more soluble in the beta phase than in the alpha phase. At room temperature, the solubility in the alpha phase is quite low. The beta phase probably acts as a getter, and it is assumed that it probably contains most of the hydrogen. The alpha phase may influence the embrittlement in that alpha-beta interfaces may provide preferred sites at which microsegregation of hydrogen and consequent embrittlement can occur.

Johnson: You said that as the temperature is raised the solubility of hydrogen in the beta phase should increase. This is contrary to data to the effect that hydrogen is absorbed exothermally. Do you mean the solubility relative to another phase?

Burte: The effects of hydrogen contamination which are characteristic of testing at room temperature disappear when testing is performed at elevated temperatures. In order to explain this behavior, it is suggested that at the elevated temperatures there is less tendency for segregation of hydrogen in the deformed material. Solubility, as used here, refers to this tendency to undergo microsegregation.

Johnson: Do you have evidence that the solubility changes with temperature?

Burte: Dr. Jaffee will show some evidence for this in his paper ("Effects of Hydrogen on the Mechanical Properties of Titanium," this report).

Margolin: Is it necessary that embrittlement occur only during straining? Can you prestrain and still get embrittlement? Can you deform at elevated temperature so that the specimen contains residual deformation, then lay it away at room temperature, and still get embrittlement?

Burte: Lt Wruck ("Creep Embrittlement of Titanium Alloys," this report) will describe an embrittling reaction, due to hydrogen, that can occur at elevated temperatures. We have not yet had time to do much work on the effects of prestrain at room temperature. Such experiments would be very interesting, and should be performed.

Crossley: At the temperature at which the distribution of hydrogen is established, the alpha phase contains an equilibrium amount of hydrogen dissolved in it. If the alpha phase does not play a role in the embrittlement, it would be because the solubility of hydrogen in the alpha phase does not change as the temperature is decreased. Do you have any information on this?

Burte: The solubility of hydrogen in the alpha phase is very markedly dependent on the temperature.

Crossley: If that is the case, hydrogen should precipitate from alpha as well as from beta.

Burte: At room temperature, there is probably very little hydrogen in solution in the alpha phase; this is why it is assumed that microsegregation in the alpha phase is not very important.

Kotfila: I don't think we will be able to answer all of your questions about the details of a mechanism of hydrogen embrittlement; we don't claim to have the answers. Lt Burte merely presented an hypothesis based on the data now available; we hope it will stimulate more work, because more research is definitely needed. We have been working on hydrogen embrittlement in steel for many years and haven't solved it yet, so I think it may take a little time to solve the problems involved in hydrogen embrittlement in titanium.

Durfee: Did you get good pictures of any titanium hydride?

Burte: We do have photomicrographs of the deformed material (near fracture in a test specimen) which show a dark featherlike component similiar to what others have seen. We have not yet done enough to say very much about it. We have not yet identified any hydride phase.

Fredrickson: Do you have any indications of the effects of contamination by iron on the hydrogen tolerance of alloys which do not nominally contain iron?

Burte: Not for alpha-beta alloys.

Folk: Have you arrived at any formula by which you can predict the stress level at which notch stress rupture testing should take place?

Burte: There is no simple formula, and we do not yet have a complete picture. I think that a presentation of our latest thinking on the use of room temperature rupture testing, considering both notched and unnotched specimens, will be helpful.

The rupture tests provide us with two criteria for susceptibility to embrittlement at a given hydrogen level: time to fracture, and type of fracture, brittle or ductile.

The highest stress at which we can perform a rupture test is approximately the ultimate tensile strength. At high stress levels, near the ultimate tensile strength, both hydrogen contaminated and very low hydrogen specimens fracture in relatively short times. If the time to fracture is short enough the hydrogen contaminated as well as the very low hydrogen specimens may fracture in a relatively ductile manner. The effects of such an overload are illustrated in Figure 4 and Table 12 for notched specimens, and in Table 5 for unnotched specimens.

As the stress level is decreased the time to fracture is increased, however, it is increased much more rapidly for very low hydrogen specimens. At intermediate stress levels the very low hydrogen specimens do not fracture in time periods of practical interest, while the hydrogen contaminated specimens do fracture. As the stress level is decreased the hydrogen contaminated specimens fracture in a more and more brittle manner (See Table 4 and Figure 4). It should be noted that the time to fracture of hydrogen contaminated specimens depends upon the hydrogen level (see Figure 3). As the hydrogen level is decreased, the time to fracture, at a given stress level, is greatly increased.

At very low stresses (underloading) even the high hydrogen specimens do not fracture in time periods of practical interest. For a given alloy, the stress below which fracture will not occur in 1000 hours probably increases as the hydrogen level decreases.

Thus, between the extremes of overloading and underloading there is an intermediate range of stress levels at which hydrogen contaminated specimens can fail prematurely, in a brittle manner, in times of less than 1000 hours. This range of stress is much greater for notched specimens than for unnotched specimens. However, with unnotched specimens a much more accurate measurement of the reduction in area at fracture is possible.

The stress level below which a hydrogen free specimen will not fracture in a specified time is of obvious interest. If it is known, the necessity of testing vacuum annealed control specimens is eliminated. It will probably depend upon the material being tested, the type of sample used, and the manner in which the rupture tests are performed. Our test results are not yet sufficiently extensive to specify such stress levels.

With this as a background I would first like to consider two cases in which the object of the rupture test is to show, in the simplest manner possible, that the material at a certain hydrogen level is susceptible to embrittlement.

a. Very high hydrogen level. In a very schematic way Figure 29a shows the relationship between the stress versus time to fracture curves for rupture tests on notched versus unnotched specimens. For the notched specimens, short time (24 hour) premature brittle fracture will occur over a wide range of stresses. It is easy to choose a relatively low stress at which a hydrogen free specimen would not fracture in 1000 hours, but at which the very high hydrogen specimen will fracture in a short time. Performing the rupture test at such a stress level on a notched specimen would obviate the necessity for testing a vacuum annealed control specimen. (Our experience indicates that in this case, the unnotched tensile strength is a useful stress level at which notched specimens can be loaded.)

b. Intermediate hydrogen levels. Figure 29b shows the schematic relationship between the stress versus time to fracture curves for material at an intermediate hydrogen level. Naturally we want to perform the rupture test in such a manner that it requires the least time. As the hydrogen level decreases the time to fracture at a given stress increases. Therefore we would want to perform the test at a higher stress than was used in the previous case (very high hydrogen level). However, if stress is increased very much, the behavior of the hydrogen contaminated material begins to approach that of hydrogen free material in both time to fracture and ductility of fracture. It might become necessary to test a vacuum annealed control sample. As previously pointed out we will eventually reach an upper stress limit at which the rupture test cannot be used to differentiate between high and low hydrogen material. Although few data are available, it is not unreasonable to assume that at lower hydrogen levels we must use lower stresses and longer times to fracture in order to obtain the premature brittle fractures which are indicative of hydrogen embrittlement. It must also be remembered that the lower stress limit is probably increasing as hydrogen content decreases. Therefore, the range of stress levels suitable for detecting a tendency towards hydrogen embrittlement probably becomes smaller as the hydrogen content decreases.

The curves in Figure 29 represent the range over which premature brittle fracture are obtained. In the experiments on cylindrical specimens performed to date, we have seen no evidence that a premature brittle fracture can be obtained in a shorter time with a notched specimen than with an unnotched specimen.

As the hydrogen level is reduced it is reasonable to assume that the material will show evidence of embrittlement only under more and more severe conditions. The designer must now ask himself whether he is willing to use material with a hydrogen content such that it shows any tendency at all towards embrittlement. If his answer is no, the problem becomes one of showing that the material is not subject to embrittlement, rather than the relatively simpler problem of demonstrating that it is susceptible to embrittlement at a higher hydrogen level. Determining the best way of doing this, and determining how closely the vacuum annealed state must be approached in order to obtain ductile behavior will require much more work than we have done up to now. I would like to suggest that the best evidence for absence of a tendency towards hydrogen embrittlement is if the reduction in area of the hydrogen contaminated specimen, tested at an exceedingly slow rate of deformation, is the same as that for a hydrogen free specimen. The rate of deformation should be so slow that fracture requires several hundred hours; therefore the use of tensile test equipment would be impractical. Since ductility can be measured more accurately for unnotched specimens than for notched specimens, the former are suggested. Perhaps the following test would be useful: an unnotched specimen is initially loaded at a stress below the yield strength; after specified time intervals small fixed increments of load are added; the rate of adding load is such that a hydrogen free specimen would fracture in several hundred hours. The parameters to be measured would be stress and total time at which fracture occurs, and elongation and reduction in area. This is merely a suggestion, however, since we have not actually performed such a test. Test procedures such as this would be quite expensive and could not be used for routine acceptance testing. The best practice will be to keep the hydrogen content well below a predetermined tolerance limit.

Durfee: In the manufacture of turbine wheels from vacuum annealed material and not vacuum annealed material we have noted that there is a tendency for more warpage in vacuum annealed material. This warpage apparently occurs on cooling to room temperature. I was wondering about the creep strength of vacuum annealed material at temperatures of say 1200 to 1300°F? I would also be curious to know whether vacuum annealing caused a drop in yield and tensile strength.

Kotfila: We have not yet investigated the effects of hydrogen contamination on creep strength, but we are planning to do so, probably through one of our contractors.

Burte: Vacuum annealing for 24 hours at 1200 to 1300°F does sometimes cause a decrease in strength. These changes are small and are expected since the as-received barstock is not always in a dead annealed state.

Folk: Has any thought been given to the problem of how specimen preparation might affect the results?

Klinger: I think that careful specimen preparation is important for work such as this. All of the specimens were prepared in the same machine shop under the same conditions.

Burte: We cannot yet say what is the best method of specimen preparation; some work along these lines is now in progress. In our work we were interested in comparisons between two or more hydrogen levels, and as Mr. Klinger pointed out specimens for these comparisons were prepared in quite comparable manners. I doubt if an interaction between hydrogen level and the manner of specimen preparation is affecting our results. We used several types of specimen in our tests on sheet and barstock, and the general effects of hydrogen embrittlement were always the same.

Dore: Does the microsegregation cause crack initiation or propagation?

Burte: The microsegregation is assumed to provide a place where microcracks can start; precipitation of a hydride phase is one possibility. Under the influence of the applied stress the cracks will propagate, eventually causing the specimen to fracture.

Dore: In other words it is just a stress raiser?

Burte: Yes.

Dore: I thought it might be due to expansion of the lattice.

Burte: That is quite possible. I don't think we can say yet exactly how the microsegregation causes a crack to form. A hydride precipitate causing a stress raiser is merely offered as an illustrative possibility. Once a microcrack has formed in hydrogen contaminated material, progressive embrittlement at the root of the microcrack should facilitate its propagation.

Finlay: Some of the materials that you reported on were undoubtedly melted quite a bit earlier than some of the others, and may have had higher oxygen contents. Are there any data available on how the other interstitials effect hydrogen embrittlement? Do you plan to get such information for the materials which you tested?

Burte: Complete chemical analyses are now being obtained for all the materials which were tested. I don't think we have tested enough different heats to be able to say how contamination by the other interstitials affects hydrogen tolerance.

Kotfila: We are quite cognizant of the fact that interstitial level may affect hydrogen tolerance. Thermal history is also quite important.

Hill: Did you obtain grain boundry failures or clevage failures in the rupture test specimens which failed with very low reductions in area?

Burte: We don't know yet, but we hope to have this information relatively soon. It is not an easy determination, since in many of these alloys the microstructure is very fine.

Anonymous: Is there enough information to determine whether there is a greater tendency towards embrittlement at low base ductility levels than at higher base ductility levels. I think that if this is the case you will have a nice simplification of the effects of heat treatment, interstitials, and other factors that may cause trouble.

Burte: We are, of course, looking for such a simplification, but I don't think we have enough information to say what the story is. In heat treatment there should be other variables. Thus the number of sites at which embrittlement can occur may depend upon the extent of interfacial area between the alpha and beta phases.

TABLE 1

ANALYSES OF MATERIALS INVESTIGATED

Mat'ls Lab. Code.	Alloy	Heat	Source*	Analysis by	As-Received Analysis								
					Al	Fe	Cr	Mo	Mn	C	N	V	H** (ppm)
D	Ti-140A	M1170	TMC	Vendor		2.26	2.35	1.76		0.06	0.02		250
Z	Ti-140A	M1192	TMC	Vendor		2.07	2.00	1.97		0.06	0.02		210
F	Ti-150A	R68	TMC	Mat'ls Lab.		1.09	3.20			0.15	0.08		250
P	Ti-150A	M308	TMC	Vendor		1.51	2.60			0.04	0.09		160
G	Ti-155AX	Unknown	TMC	Mat'ls Lab.	5.27	1.64	1.59	1.0		0.08	0.02		260
K	RC-130B	B5038	RC	Vendor	5.0				4.5	<0.1	0.04		60
R	RC-130B	B3371	RC	Vendor	4.3				4.6	<0.1	0.05		60
J	Ti-6Al-4V		Armour	Vendor	6.36							4.27	160

* TMC = Titanium Metal Corporation of America
RC = Rem-Cru Titanium Incorporated
Armour = Armour Research Foundation

** The hydrogen analyses were performed by Battelle Memorial Institute

TABLE 2

TENSILE PROPERTIES OF MATERIALS INVESTIGATED, AS-RECEIVED CONDITION
ROOM TEMPERATURE FAST STRAIN RATE TENSILE TESTS ON UNNOTCHED SPECIMENS

Alloy	Heat	Ultimate Tensile Strength (1000 psi)	Yield Strength 0.2% Offset (1000 psi)	% Elongation in 4D	% Reduction in Area
Ti-140A	M1170	143	133	23	59
Ti-140A	M1192	134	120	24	62
Ti-150A	R68	152	139	19	52
Ti-150A	M308	157	149	25	59
Ti-155AX	Unknown	171	156	16	48
RC-130B	B5038	147	123	17	42
RC-130B	B3371	136	122	17	38
Ti-6Al-4V		155	128	15	44

TABLE 3

PREPARATORY TREATMENTS

Alloy and Heat	As-received hydrogen level (ppm)	Hydrogen level tested (ppm)	Treatment applied to the as-received material
Ti-140A Ht. M1170	250	20	Vacuum anneal, 1200°F, 24 hrs. + furnace cool
		170	Vacuum anneal, 1200°F, 2 hrs. + air cool + thermal treat in argon, 1200°F, 22 hrs. + furnace cool
		250	Thermal treat in helium, 1200°F, 24 hrs. + furnace cool.
Ti-140A Ht. M1192	210	210	Thermal treat in air 1200°F, 24 hrs. + furnace cool
		210	Thermal treat in air 1200°F, 24 hrs. + furnace cool + thermal treat in air 1350°F, 22 hrs. + air cool.
Ti-150A Ht. R68	250	10	Vacuum anneal, 1300°F, 25 hrs. + furnace cool
		250	Thermal treat in air, 1300°F, 24 hrs. + furnace cool.
Ti-150A Ht. M308	160	30	Vacuum anneal, 1200°F, 24 hrs. + furnace cool
		160	No further treatment
Ti-155AX	260	5	Thermal treat in air, 1250°F, 0.5 hrs. + furnace cool + vacuum anneal, 1300°F, 24 hrs. + furnace cool.
		260	Thermal treat in air, 1250°F, 0.5 hrs. + furnace cool + thermal treat in air, 1300°F, 24 hrs. + furnace cool.
RC-130B Ht. B5038	60	10	Vacuum anneal, 1300°F, 25 hrs. + furnace cool
		320	Hydrogenate, 1300°F, 21 hrs. + air cool + thermal treat in air, 1300°F, 4 hrs. + furnace cool.

TABLE 3 (cont'd)
PREPARATORY TREATMENTS

Alloy and Heat	As-received hydrogen level (ppm)	Hydrogen level tested (ppm)	Treatment applied to the as-received material
RC-130B Ht. B3371	60	60	Thermal treat in air, 1300°F, 3 hrs. + furnace cool
		150	Hydrogenate, 1300°F, 21 hrs. + air cool + thermal treat in helium, 1300°F, 5 hrs. + furnace cool.
		190	Hydrogenate, 1300°F, 21 hrs. + air cool + thermal treat in helium, 1300°F, 5 hrs. + furnace cool.
		280	Hydrogenate, 1300°F, 21 hrs. + air cool + thermal treat in helium, 1300°F, 5 hrs. + furnace cool.
Ti-6Al-4V	160	5	Vacuum anneal, 1300°F, 24 hrs. + furnace cool.
		270	Hydrogenate, 1300°F, 21 hrs. + air cool + thermal treat in air, 1300°F, 4 hrs. + furnace cool.

NOTES

1. Hydrogenations were performed by Battelle Memorial Institute in a Sieverts type apparatus

2. During vacuum annealing, the pressure, measured in a room temperature zone in the system, was usually below 0.1 micron.

TABLE 4

ROOM TEMPERATURE RUPTURE TESTS ON UNNOTCHED SPECIMENS

RC-130B, Ht. B5038

Hydrogen level = 320 ppm

Stress (1000 psi)	Time to Fracture (hrs.)	% R. A. at Fracture
143	1.3	11.8
136	9.0	8.6
129	22	5.4
123	442	2.6

TABLE 5

ROOM TEMPERATURE RUPTURE TESTS ON UNNOTCHED SPECIMENS

Ti-140A, Ht. M1170

Hydrogen Level (ppm)	Stress (1000 psi)	Time to Fracture (hrs.)	% R. A. At Fracture
20	137	0.4	52
	118	>803	-
250	138	0.1	19
	119	2.4	3
	101	>1244	-
170	129	2.5	13.1

TABLE 6

RUPTURE AND TENSILE TESTS AT 600°F ON UNNOTCHED SPECIMENS

Ti-140A, Ht. M1170

Hydrogen Level (ppm)	Test	Stress (1000 psi)	Time to Fracture (hrs.)	% R. A. at Fracture
20	Tensile	93	-	60
	Rupture	90	>946	-
250	Tensile	92	-	62
	Rupture	90	>987	-

TABLE 7

RUPTURE TESTS ON NOTCHED SPECIMENS

Ti-140A, Ht. M1170

Hydrogen Level (ppm)	Test Temperature (°F)	Stress (1000 psi)	Time to Fracture (hrs.)
20	72	100	>1224
	200	111	>1175
250	72	98	4
	200	111	>917

TABLE 8

ROOM TEMPERATURE RUPTURE TESTS ON NOTCHED SPECIMENS

Ti-140A, Ht. M1170

Hydrogen Level (ppm)	Stress (1000 psi)	Time to Fracture (hrs.)	% R. A. at Fracture
20	227	Tensile Test	6.6
	135	> 446	-
170	156	10.5	3.5
	136	71	1.2
	129	334	2.4
250	133	0.7	1.0
	114	1.7	1.9
	98	4	9.4

TABLE 9

ROOM TEMPERATURE RUPTURE TESTS ON NOTCHED SPECIMENS

Ti-140A, Ht. M1192
Hydrogen level = 210 ppm

Condition	Stress (1000 psi)	Time to Fracture (hrs.)
Furnace cooled from 1200°F	170	1.0
	145	4.0
Air cooled from 1350°F	170	> 93
	145	>300

TABLE 10

ROOM TEMPERATURE RUPTURE TESTS ON UNNOTCHED SPECIMENS

Ti-150A, Ht. R68

Hydrogen Level (ppm)	Stress (1000 psi)	Time to Fracture (hrs.)	% R. A. at Fracture
10	144	1.3	65.0
	137	18	57.3
250	142	0.5	1.0
	138	1.0	0.5

TABLE 11

ROOM TEMPERATURE RUPTURE TESTS ON NOTCHED SPECIMENS

Ti-150A, Ht. R68

Hydrogen Level (ppm)	Stress (1000 psi)	Time to Fracture (hrs.)	% R. A. at Fracture
10	137	> 58	-
	81.5	>1224	-
250	136	1	0.1
	83.8	3	0.0

TABLE 12

ROOM TEMPERATURE RUPTURE TESTS ON NOTCHED SPECIMENS

Ti-150A, Ht. M308

Hydrogen Level (ppm)	Stress (1000 psi)	Time to Fracture (hrs.)	% R. A. at Fracture
30	189	75	10.2
	181	>367	-
160	191	2.8	10.4
	179	6.0	2.2
	160	4.9	0.6

TABLE 13

ROOM TEMPERATURE RUPTURE TESTS ON UNNOTCHED SPECIMENS

Ti-155AX

Hydrogen Level (ppm)	Stress (1000 psi)	Time to Fracture (hrs.)	% R. A. at Fracture
5	158	1.2	43.2
	153	>1204	-
260	156	105.6	42.9
	155	>1204	-

TABLE 14

ROOM TEMPERATURE RUPTURE TESTS ON NOTCHED SPECIMENS

Ti-155AX

Hydrogen Level (ppm)	Stress (1000 psi)	Time to Fracture* (hrs.)
5	176	> 652
	152	>1204
260	176	> 652
	151	>1204

* No Specimens Fractured.

TABLE 15

ROOM TEMPERATURE RUPTURE TESTS ON UNNOTCHED SPECIMENS

RC-130B, Ht. B5038

Hydrogen Level (ppm)	Stress (1000 psi)	Time to Fracture (hrs.)	% R. A. at Fracture
10	137	2.3	45.6
	129	>1240	-
320	136	9.0	8.6
	129	22.1	5.4

TABLE 16

ROOM TEMPERATURE RUPTURE TESTS ON NOTCHED SPECIMENS

RC-130B, Ht. B3371
Stress ~ 152,000 psi

Hydrogen Level (ppm)	Time to Fracture (hrs.)
60	>113
150	14.1
190	3.1
280	1.9

TABLE 17

ROOM TEMPERATURE RUPTURE TESTS ON UNNOTCHED SPECIMENS

Ti-6Al-4V

Hydrogen Level (ppm)	Stress (1000 psi)	Time to Fracture (hrs.)	% R. A. at Fracture
5	150	0.15	31
	150	> 1461	-
270	152	> 278	-
	147	> 1461	-

TABLE 18

ROOM TEMPERATURE RUPTURE TESTS ON NOTCHED SPECIMENS

Ti-6Al-4V

Hydrogen Level (ppm)	Stress (1000 psi)	Time to Fracture* (hrs.)
5	149	> 1461
	174	> 652
270	144	> 1461
	167	> 652

* No Specimens Fractured.

TABLE 19

SUMMARY

Mat'ls Lab. Code.	Alloy and Heat	Hydrogen Level (ppm)	Is Embrittlement Indicated ?
D	Ti-140A, Ht. M1170	170	yes
Z	Ti-140A, Ht. M1192	210	yes
F	Ti-150A, Ht. R68	250	yes
P	Ti-150A, Ht. M308	160	yes
G	Ti-155AX	260	no
K	RC-130B, Ht. B5038	320	yes
R	RC-130B, Ht. B3371	150	yes
J	Ti-6Al-4V	270	no

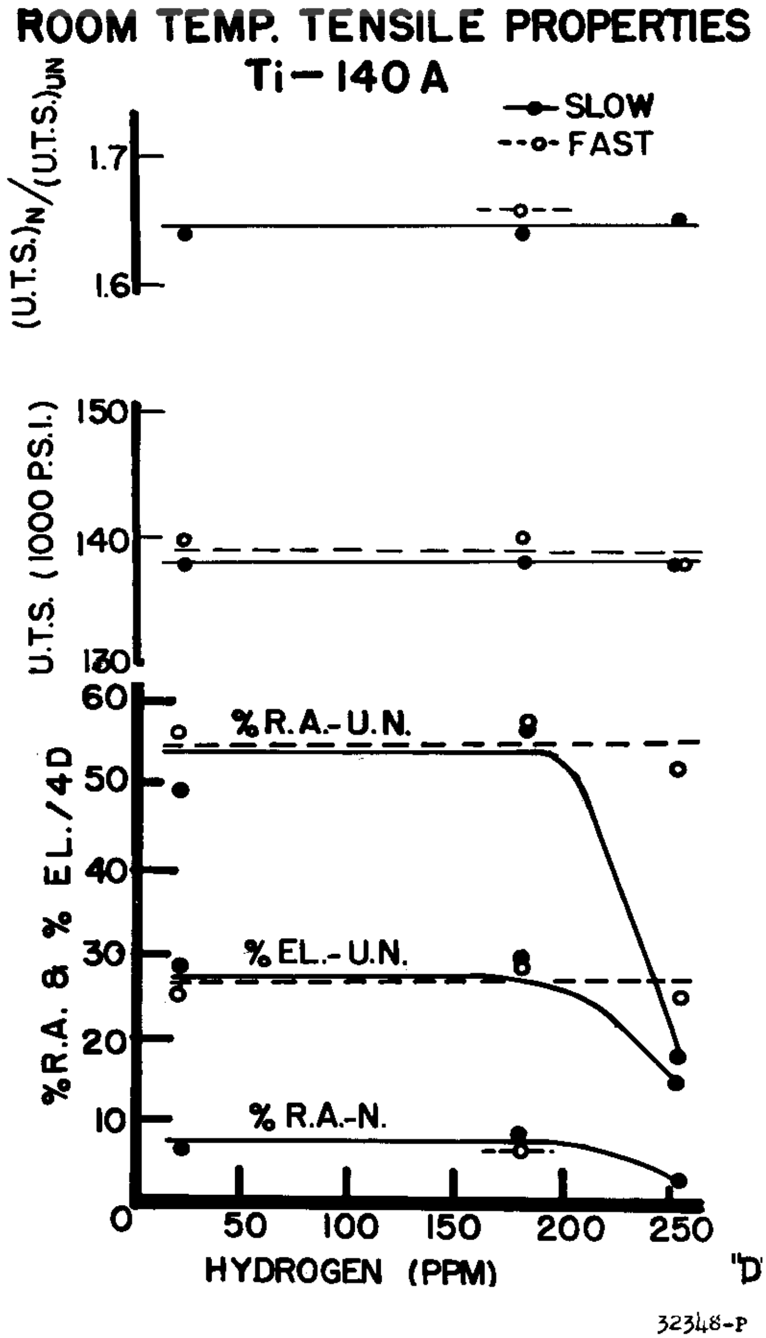


Figure 1

The effects of hydrogen on the room temperature tensile properties of Ti-140A, Ht. M1170. UN= unnotched specimen, N= notched specimen

Slow rate = 0.02 inch/min.
Fast rate = 0.10 inch/min.

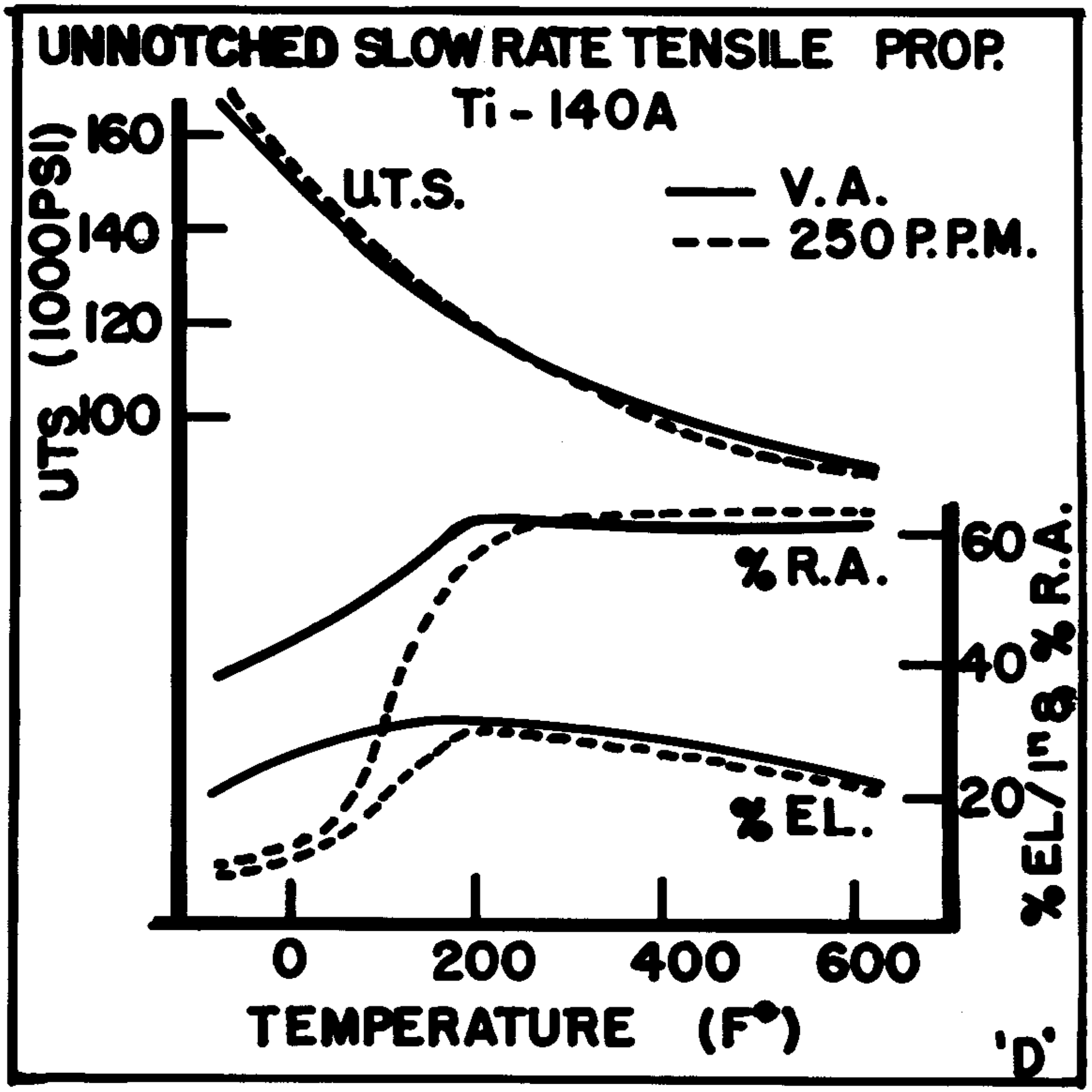


Figure 2

The effects of hydrogen on the tensile properties of Ti-140A, Ht. M1170, measured at various temperatures. V.A. = vacuum annealed= 20 ppm

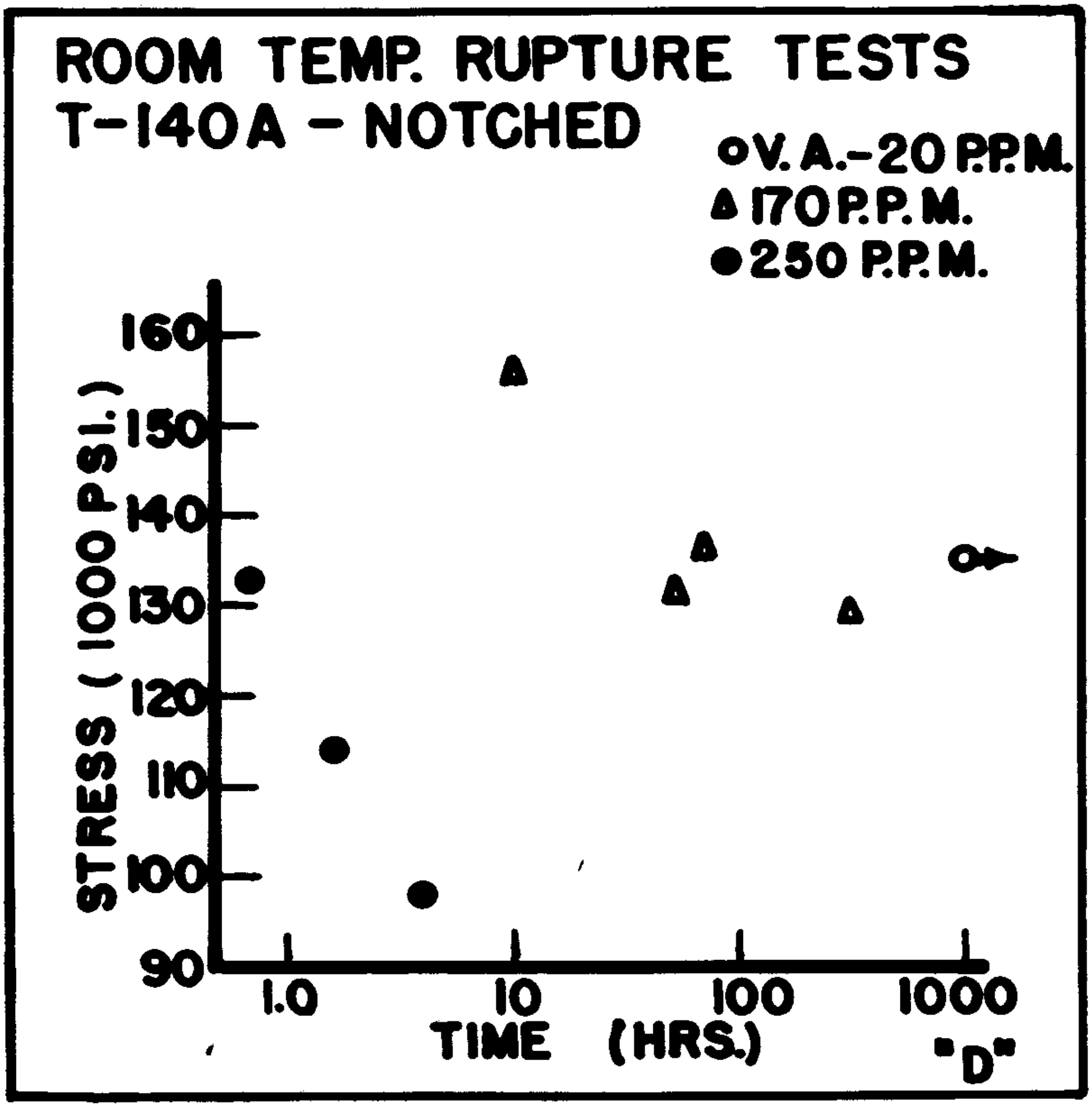


Figure 3

Room temperature rupture tests on notched specimens. Ti-140A, Ht. M1170

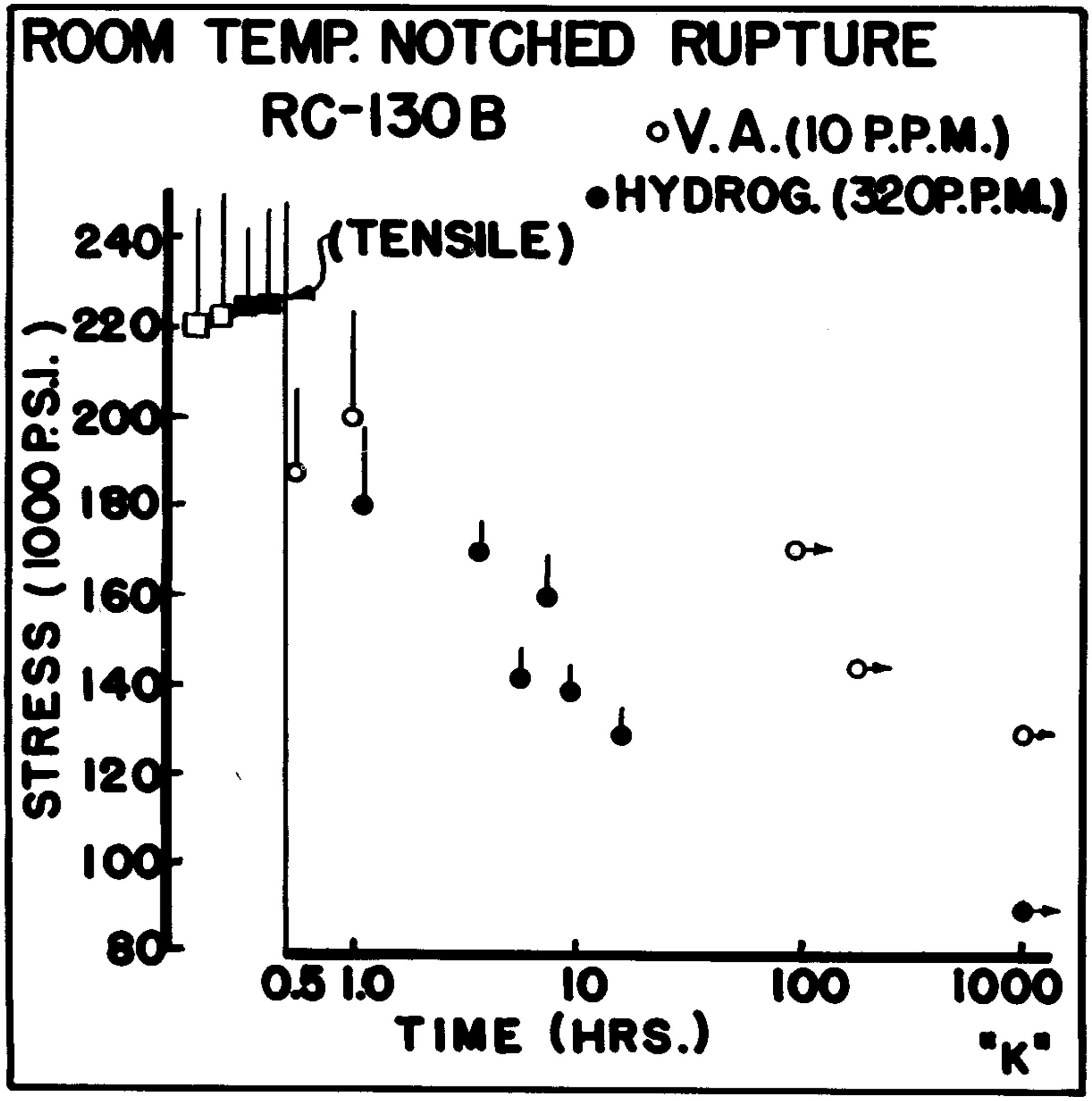


Figure 4

Room temperature tensile and rupture tests on notched specimens. RC-130B, Ht. B5038. The height of the vertical line rising from a point is proportional to the reduction in area at fracture.

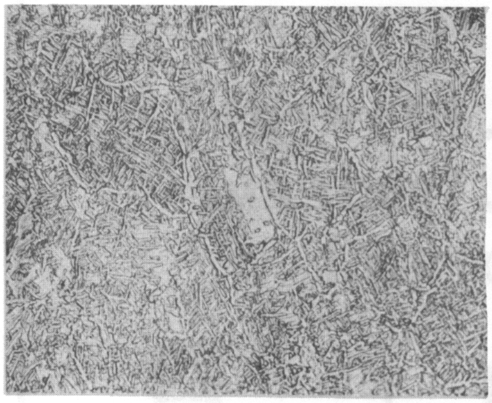


Fig 5 Photomicrograph of Ti-140A, Ht. M1170, 20ppm Mag.500X Etchant: 2 HF, 10 HNO_3, 88 H_2O

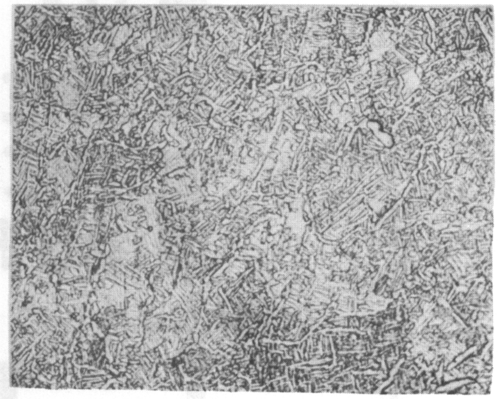


Fig 6 Photomicrograph of Ti-140A, Ht. M1170, 170ppm Mag. 500X Etchant: 2 HF, 10 HNO_3, 88 H_2O

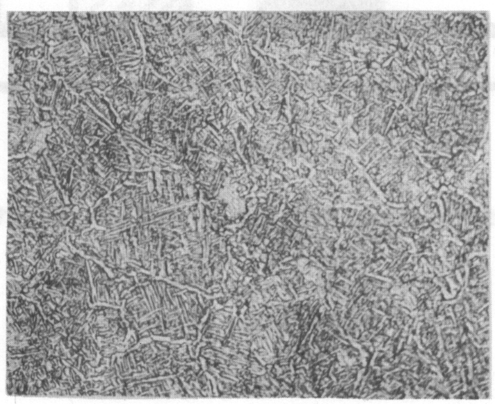


Fig 7 Photomicrograph of Ti-140A, Ht. M1170, 250ppm Mag. 500X Etchant: 2 HF, 10 HNO_3, 88 H_2O

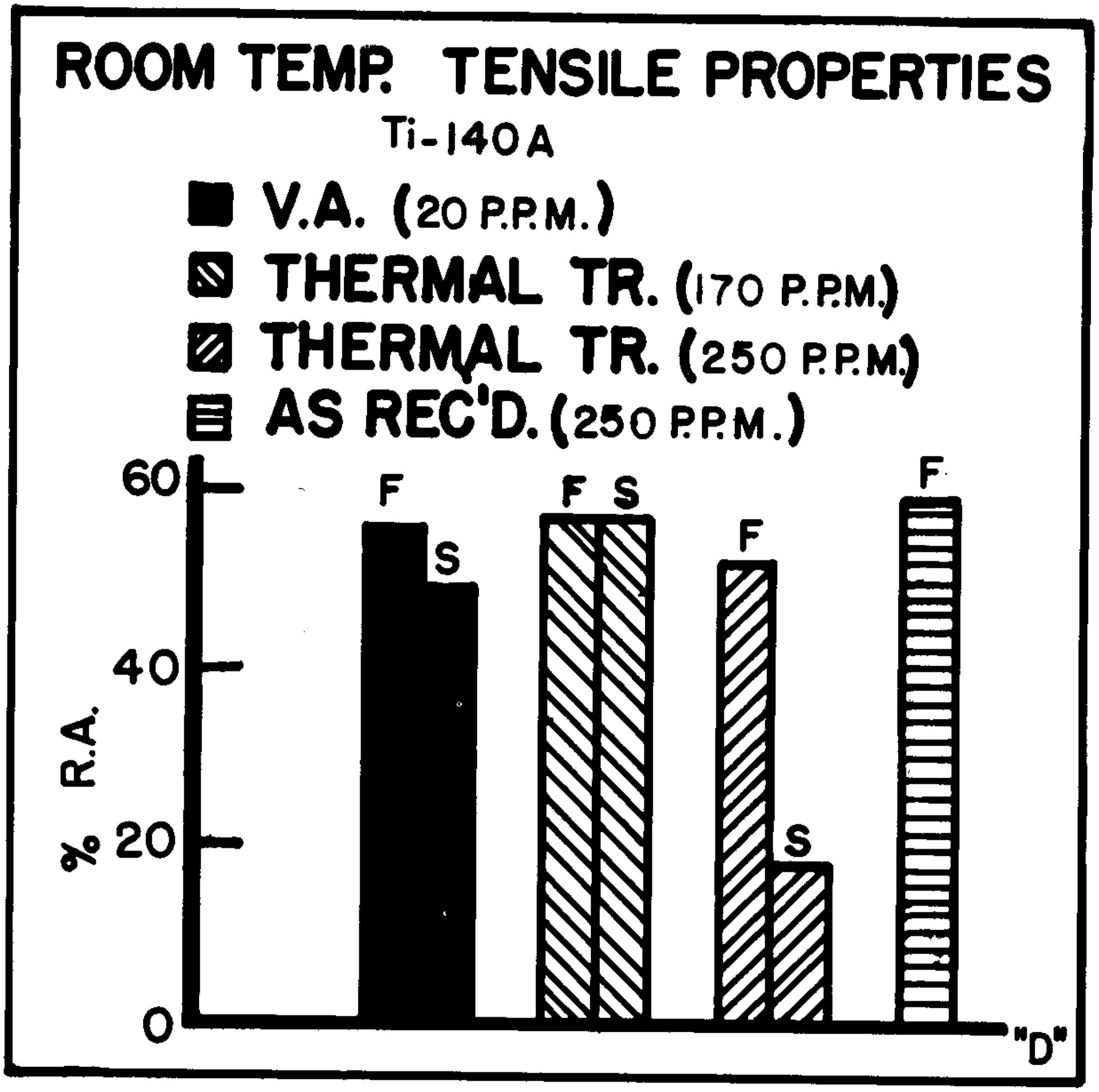


Figure 8

Room temperature tensile tests on unnotched specimens
Ti-140A, Ht. M1170
F = fast rate tensile test
S = slow rate tensile test

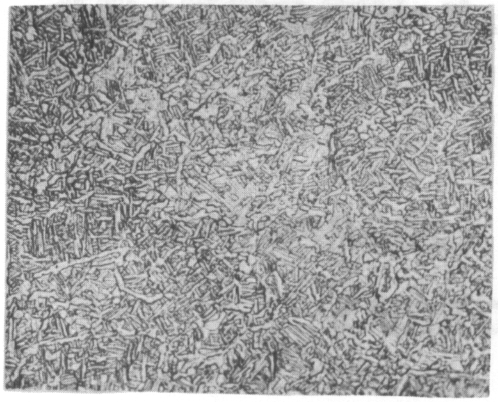


Fig 9 Photomicrograph of Ti-140A, Ht. M1192, 210ppm 1200°F + FC. Mag. 500X Etchant: 2HF, 98 H_2O

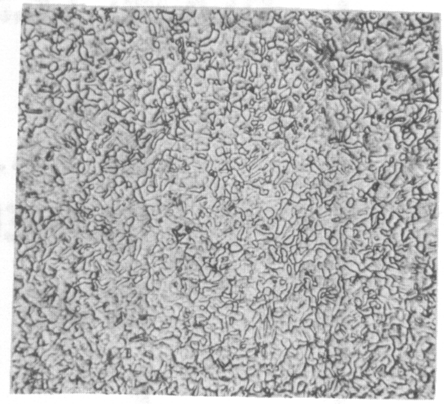


Fig 10 Photomicrograph of Ti-140A, Ht. M1192, 210ppm 1350°F + AC Mag. 500X Etchant: 2HF, 98 H_2O

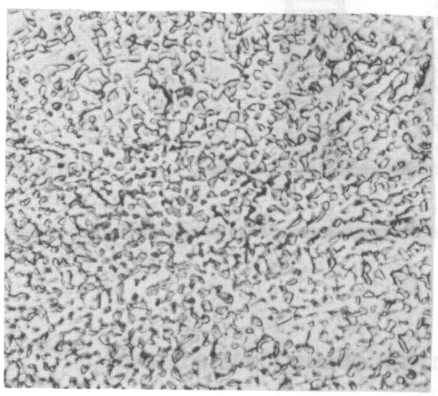


Fig 11 Photomicrograph of Ti-150A, Ht. R68, 10 ppm Mag. 500X Etchant: 1 HF, 1 HNO_3, 3 Glycerine

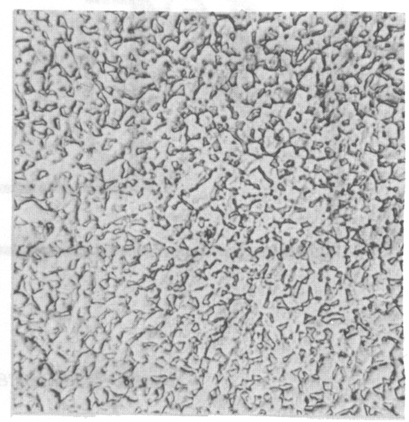


Fig 12 Photomicrograph of Ti-150A, Ht. R68, 250 ppm Mag 500X Etchant: 1 HF, 1 HNO_3, 3 Glycerine

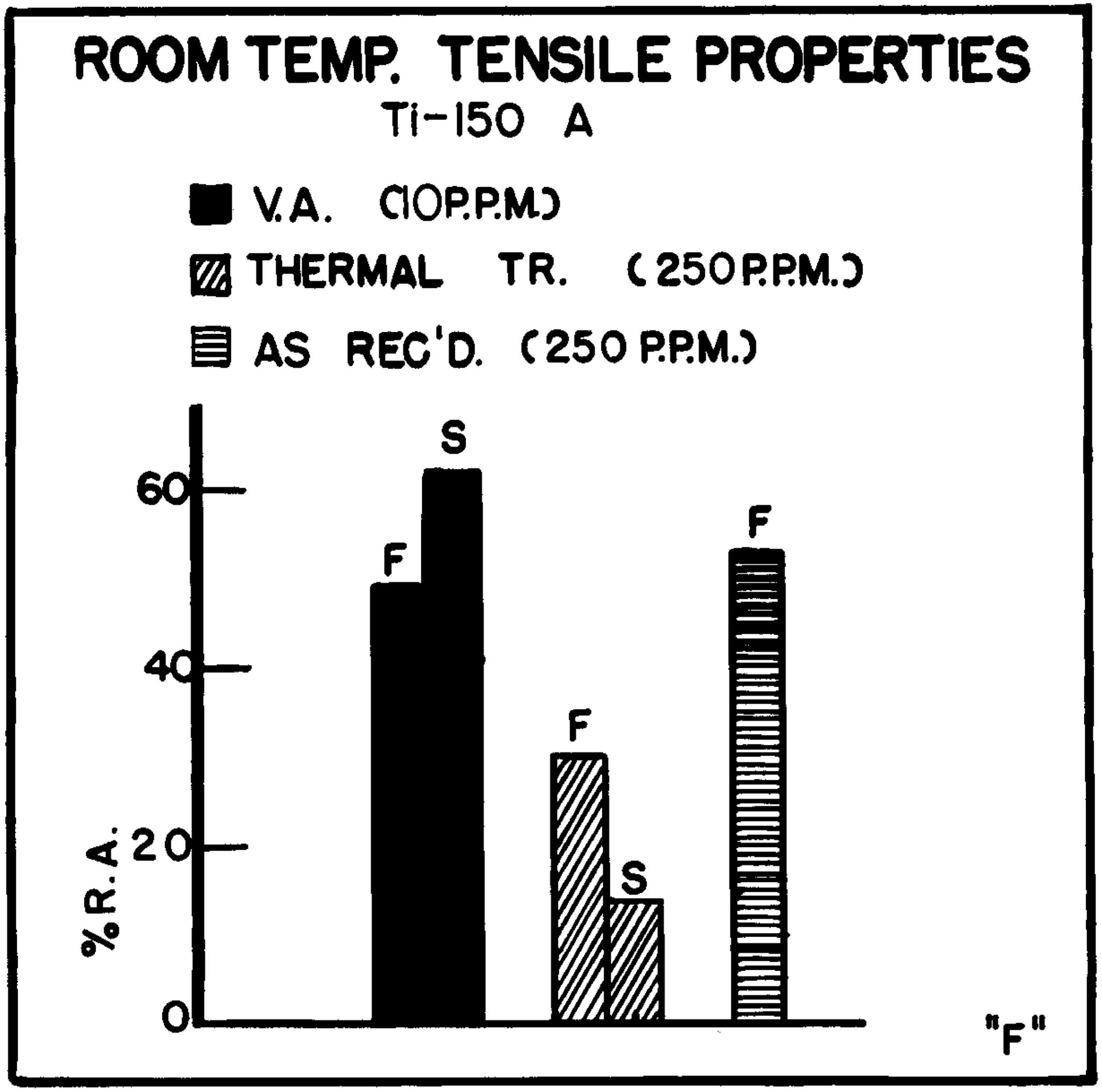


Figure 13

Room temperature tensile tests on unnotched specimens
Ti-150A, Ht. R63

F = fast rate tensile test
S = slow rate tensile test

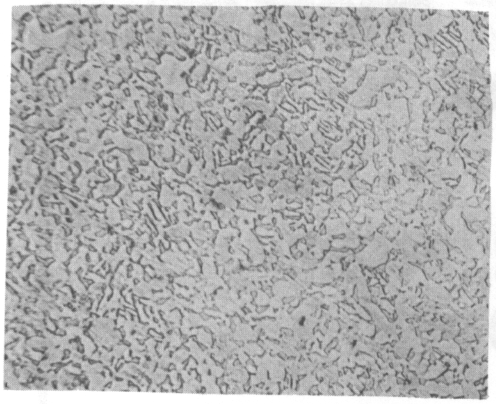


Fig 14 Photomicrograph of Ti-150A, Ht. M308, 30 ppm Mag. 500X Etchant: 1 HF, 1 HNO_3, 3 Glycerine

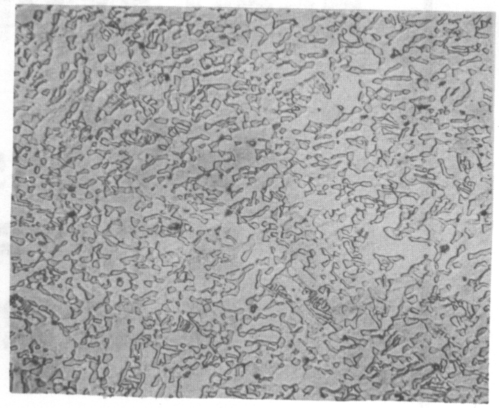


Fig 15 Photomicrograph of Ti-150A, Ht. M308, 160ppm Mag. 500X Etchant: 1 HF, 1 HNO_3, 3 Glycerine

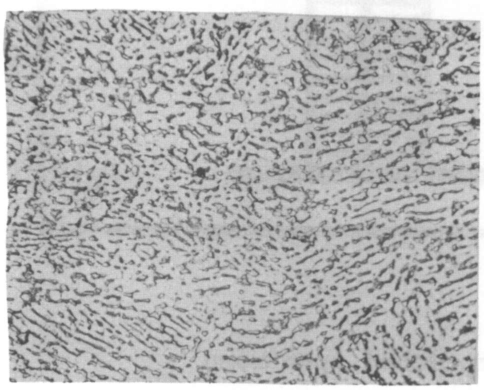


Fig 16 Photomicrograph of Ti-155AX, 5 ppm Mag.500X Etchant: 2 HF, 10 HNO_3, 88 H_2O

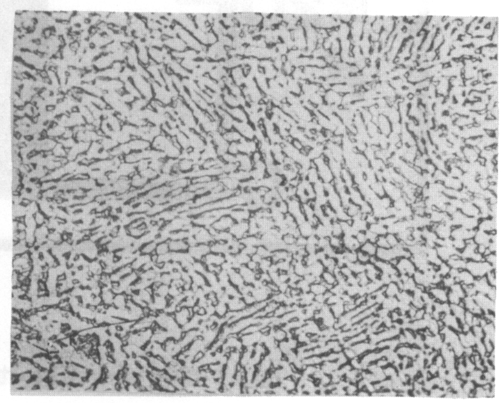


Fig 17 Photomicrograph of Ti-155AX, 260 ppm Mag.500X Etchant: 2 HF, 10 HNO_3, 88 H_2O

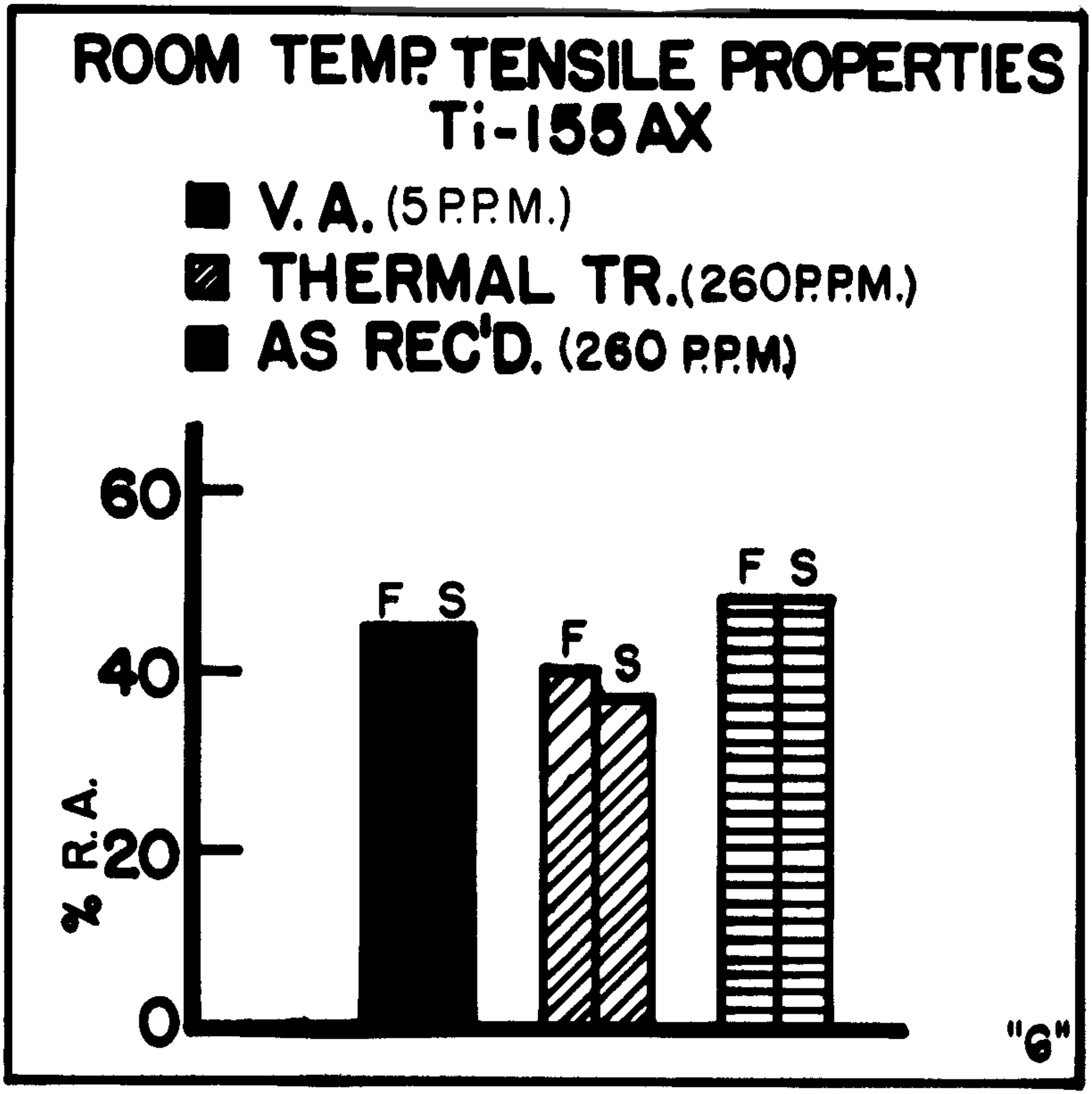


Figure 18

Room temperature tensile tests on unnotched specimens
Ti-155AX
F = fast rate tensile test
S = slow rate tensile test

Fig 19 Photomicrograph of RC-130B, Ht. B5038, 10ppm Mag. 500X Etchant: 2 HF, 10 HNO_3, 88 H_2O

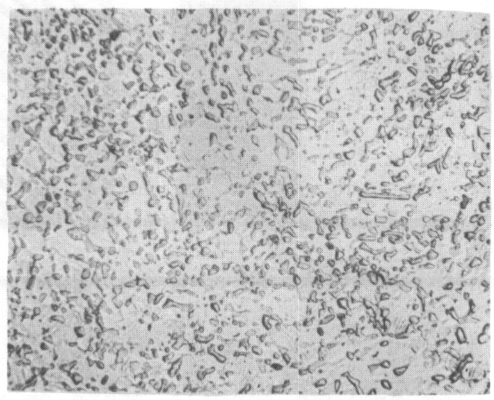


Fig 20 Photomicrograph of RC-130B, Ht. B5038,320ppm Mag. 500X Etchant: 2 HF, 10 HNO_3, 88 H_2O

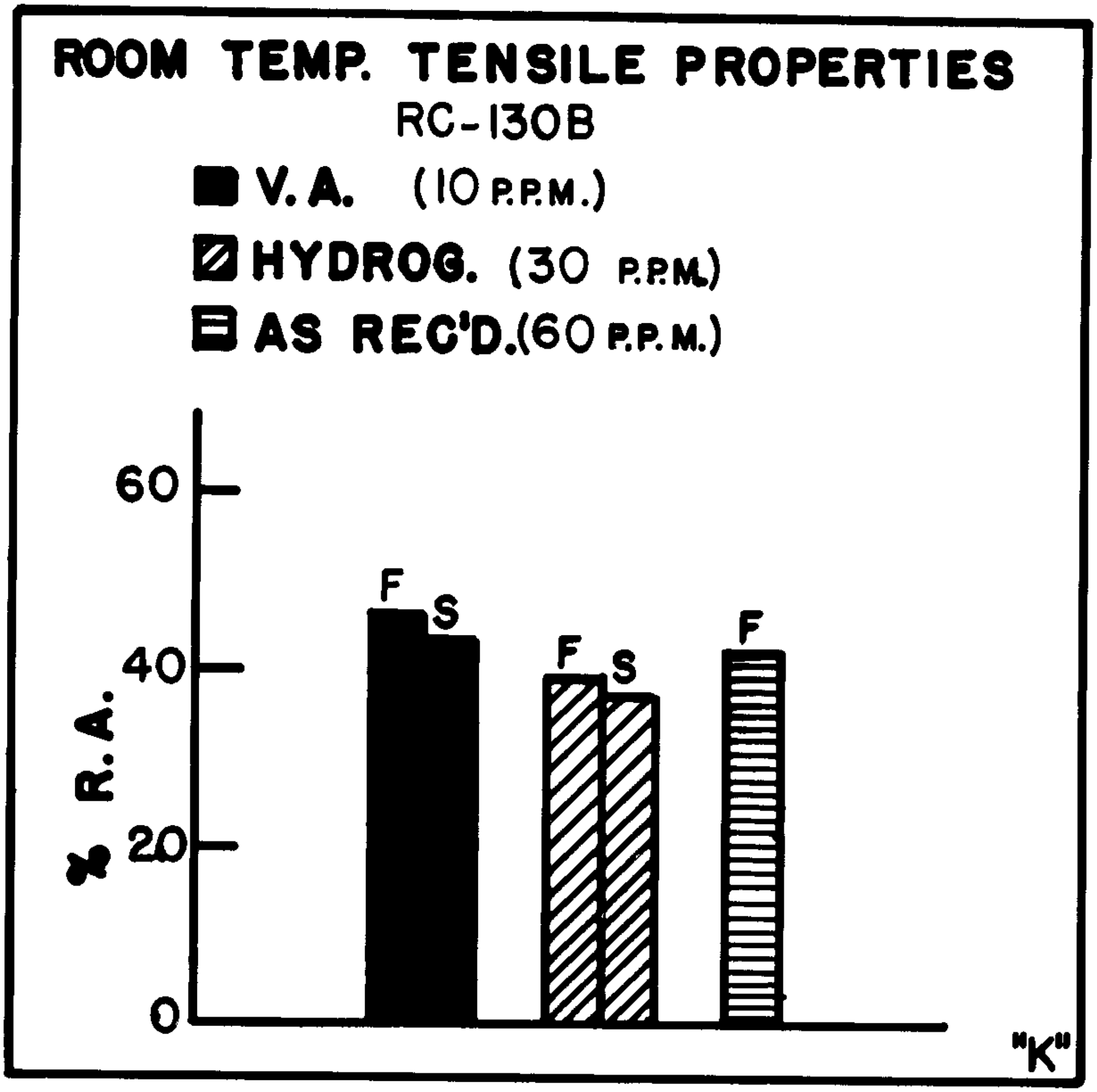


Figure 21

Room temperature tensile tests on unnotched specimens
RC-130B, Ht. B5038

F = fast rate tensile test
S = slow rate tensile test

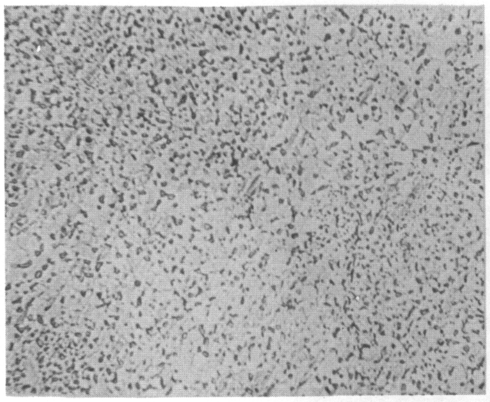


Fig 22 Photomicrograph of RC-130B, Ht. B3371, 60ppm Mag. 500X Etchant: 2 HF, 10 HNO_3, 88 H_2O

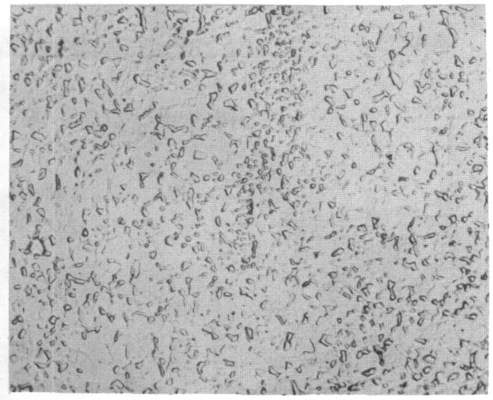


Fig 23 Photomicrograph of RC-130B, Ht. B3371,150ppm Mag.500X Etchant: 2 HF, 10 HNO_3, 88 H_2O

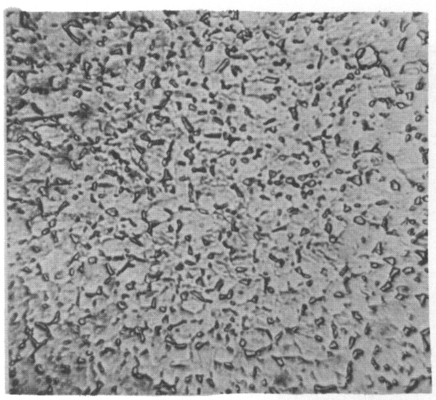


Fig 24 Photomicrograph of RC-130B, Ht. B3371,190ppm Mag. 500X Etchant: 2 HF, 10 HNO_3, 88 H_2O

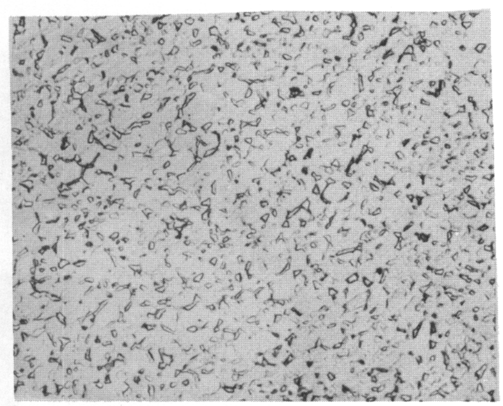


Fig 25 Photomicrograph of RC-130B, Ht. B3371,280ppm Mag. 500X Etchant: 2 HF, 10 HNO_3, 88 H_2O

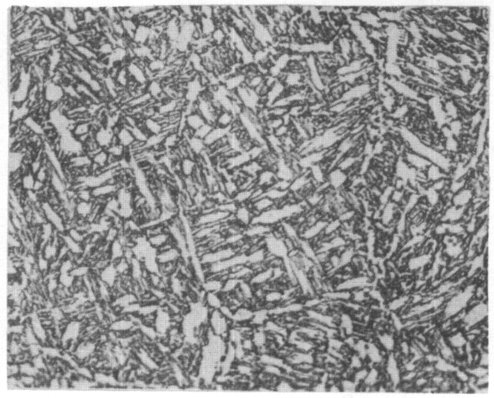


Fig 26 Photomicrograph of Ti-6Al-4V, 5 ppm Mag 500X Etchant: 2 HF, 10 HNO_3, 88 H_2O

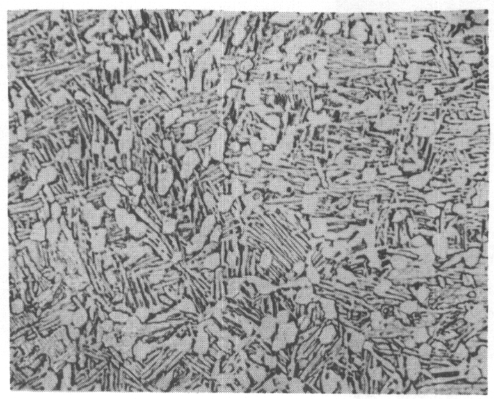


Fig 27 Photomicrograph of Ti-6Al-4V, 270 ppm Mag. 500X, Etchant: 2 HF, 10 HNO_3, 88 H_2O

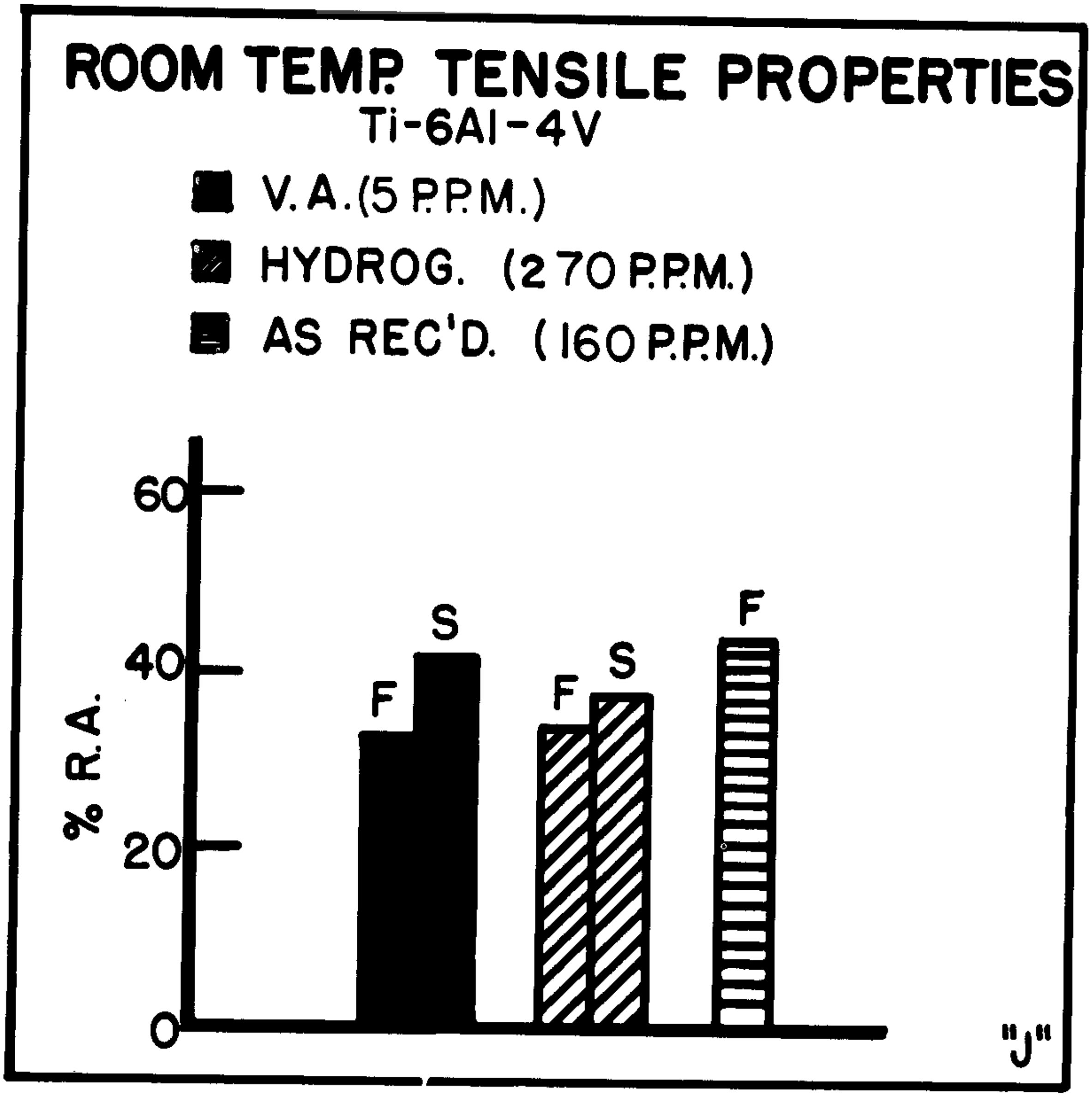


Figure 28

Room temperature tensile tests on unnotched specimens
Ti-6Al-4V
F = fast rate tensile test
S = slow rate tensile test

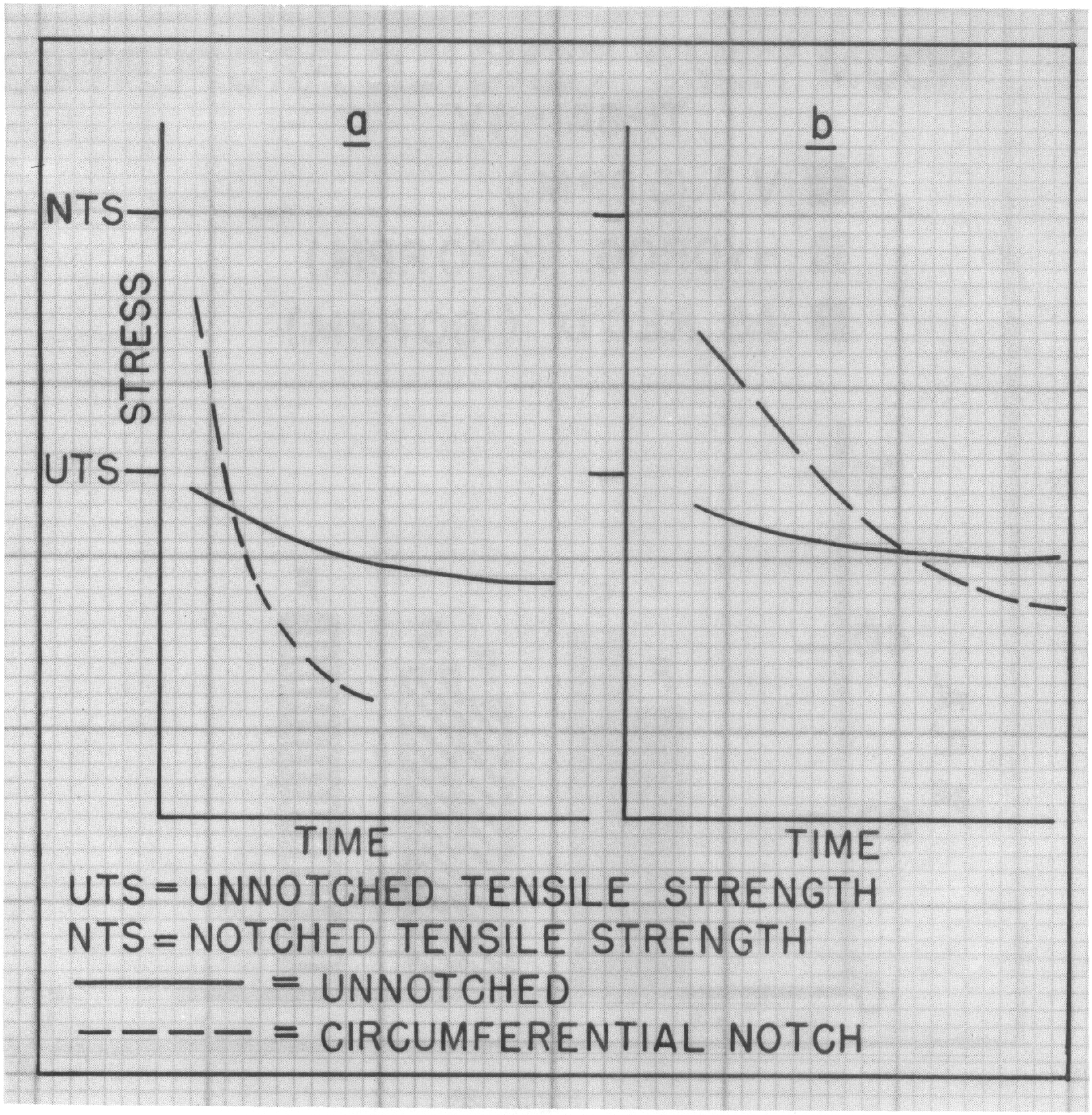


Figure 29

Schematic stress vs. time to fracture curves for room temperature rupture tests on cylindrical specimens from bar stock.

a = very high hydrogen content
b = intermediate hydrogen content

MECHANICAL PROPERTY TEST METHODS

USED FOR THE EVALUATION OF HYDROGEN EMBRITTLEMENT

by

R. F. Klinger
W. H. Rector

The existence and importance of the brittle failure of hydrogen-contaminated alpha-beta titanium alloys has been established. It has been established by mechanical tests performed under select conditions. It would therefore appear that this brittle behavior, called hydrogen embrittlement, could be detected in most cases by conducting a simple mechanical test of the correct nature. This simple test may be available in the future but for the present there exists a large problem in determining what test or tests are necessary to definitely establish the presence or absence of hydrogen embrittlement.

The approach made to the problem of the mechanical evaluation of hydrogen embrittlement by the Materials Laboratory was in the form of a broad and preliminary survey. The testing methods selected for the survey purposes were strongly based on the strain rate sensitivity of alpha-beta titanium alloys contaminated by hydrogen. It was found that the ductility of high-hydrogen-containing titanium alloys was greatly influenced by the strain rate in the ordinary room temperature tensile test. This influence was in the form of a very significant decrease in the ductility at low tensile strain rates. Since the low strain rates produced a low ductility in the high-hydrogen alloy, it was natural to go to a stress-rupture test. Here the strain rate can be reduced to a still lower value which should produce a better indication of embrittlement based on the time to failure or the ductility after failure.

The stress-rupture and tensile tests were the main methods used to evaluate hydrogen embrittlement of the alpha-beta alloys. Specimens for these tests were of several types. For tests of bar stock materials a round gage section was used in both the notched and the unnotched condition. Figure 1. This sketch shows the gage section of the notched round specimen. This specimen has a gage length of 1 inch, a diameter of .2935 inches and a 60 degree V-notch with a root diameter of .187 inches and a root radius of .01 inches. This geometry produces a theoretical stress concentration factor of about 2.7. The unnotched round specimen had a gage length of 1 inch and a diameter of .187 inches. The ends of the round specimens were 3/8 inch in diameter with 16 threads per inch. The large ratio of thread diameter to gage diameter was required to prevent brittle failure in the threads.

The sheet materials were tested using flat specimens of a thickness equal to the sheet thickness. Figure 2. This sketch shows the gage section of the notched version of the flat specimen which was used most extensively in this work. This specimen has a gage length of 1 inch, a width of .5 inches and a 60 degree V-notch with a root width of .25 inches and a root radius of .01 inches. This configuration gives a theoretical stress concentration factor of about 5.5. The unnotched flat specimen of this type consisted of a 1 inch gage length and a gage width of .25 inches. These specimens were loaded through 1/4 inch diameter holes drilled in 3/4 inch wide specimen ends.

Figure 3. This is the second type of flat specimen used. The gage section is shown with a keyhole type of notch. This gage length is 2 inches, the width 1 inch and the root width .5 inches. This type of specimen was loaded through 1/2 inch diameter holes drilled in 1 and 1/2 inch wide specimen ends. The specimens were machined after the materials received processing. The processing treatment is described in other sections of this report.

Tensile tests were conducted at room temperature, -70, 200, 400 and 600°F. All tensile tests were made in a 200,000 pound capacity Baldwin-Southwark universal testing machine using an appropriate load scale. Three different loading conditions were employed to obtain various strain or head travel rates. These rates were (1) .003 inches per inch of strain per minute to the yield strength and then .1 inches of head travel per minute to failure, (2) .02 inches of head travel per minute from zero load to failure and (3) .005 inches of head travel per minute from zero load to failure. An O. S. Peters microformer type strain pacer and a Southwark-Emery head travel pacer were used to control the rates of testing.

The low temperature tests at -70°F were made using an alcohol-dry ice bath and the elevated temperatures were obtained with a standard electrical resistance furnace. Stress-strain curves were obtained at room temperature only, using a rate of .003 inches per inch of strain per minute. The curves were made autographically with 1 and 2 inch microformer strain gages. The tensile properties determined were: yield strength, ultimate strength, elongation and reduction of area.

Stress-rupture tests were made on bar stock materials in standard lever arm type creep-rupture frames at room temperature, 150, 200, 250, 400, and 600 degrees F. and at room temperature on sheet materials. To accelerate testing, a tandem arrangement was used. In the majority of cases 4 round specimens were tested simultaneously by this method at room temperature. The stress applied was based on the tensile properties and was varied to produce different times to failure. When failures occurred in a tandem set-up, a new specimen or a dummy specimen was inserted and the stress reapplied. The elevated temperature stress-rupture tests were conducted in a more normal manner using a single specimen or two specimens in tandem. The properties obtained from the stress-rupture tests were; time to failure, elongation and reduction of area.

Another phase of the program was concerned with evaluating the effect of exposure to stress and temperature on the room temperature tensile properties. Two unnotched round specimens for each alloy condition were loaded in tandem in a standard creep-rupture frame at; room temperature, 150, 200, 250, 300, and 600 degrees F. The tandem specimens were loaded for 100 hours and then 1 specimen removed. The second specimen was reheated, reloaded and run for an additional 400 hours. The two specimens were then run in tensile tests at room temperature. The testing rate was .003 inches per inch of strain per minute to the yield strength and then .1 inches of head travel per minute to failure. The tensile properties determined in this phase of the program were yield strength, ultimate strength, elongation and reduction of area.

Figure 4. This slide shows the general relationship between the types of loading and the strain rate associated with the type of loading. The shaded portion of this figure is the area in which all of our work has been done in this program. The work has been concentrated in the lower strain rate range because the embrittlement of alpha-beta titanium alloys has been more severe at lower strain rates.

It is important to observe that the test procedures applied in this work were evolved in a crash program. Several desirable refinements of tests procedures were not included because of the limited time available. Because of this condition the scatter in results is probably greater than could be attributed to the material itself. For this same reason the absolute values of some of the properties such as the time to failure in the stress-rupture tests may not be comparable to values obtained under more refined test conditions. It is believed however that the test methods served the purpose of this work-- to show the general effect of hydrogen content on the brittle behavior of alpha-beta alloys. Some of the compromises in testing procedure which may affect scatter or the absolute value of the data are: (1) only normal precautions were taken to insure accurate alignment of notched specimens. For brittle materials eccentric loading may be critical, (2) Strain rates in some cases were controlled by a head pacer which does not provide a constant strain rate or an accurate knowledge of the strain rate. Relative values are, however, known fairly well, (3) Temperature control was less accurate than normal. Again relations rather than absolute values were desired and these relations would not be greatly affected, (4) Tandem loading produced loading and unloading cycles in all but the first specimen to fail. The effect on the remaining specimens is unknown.

In conclusion it should be noted that the objective of the test methods was to rapidly obtain a general indication of the effect of hydrogen contamination on the mechanical properties of a number of alpha-beta alloys. This objective has been accomplished. Now, as time permits, gaps or unexplainable variations can be checked.

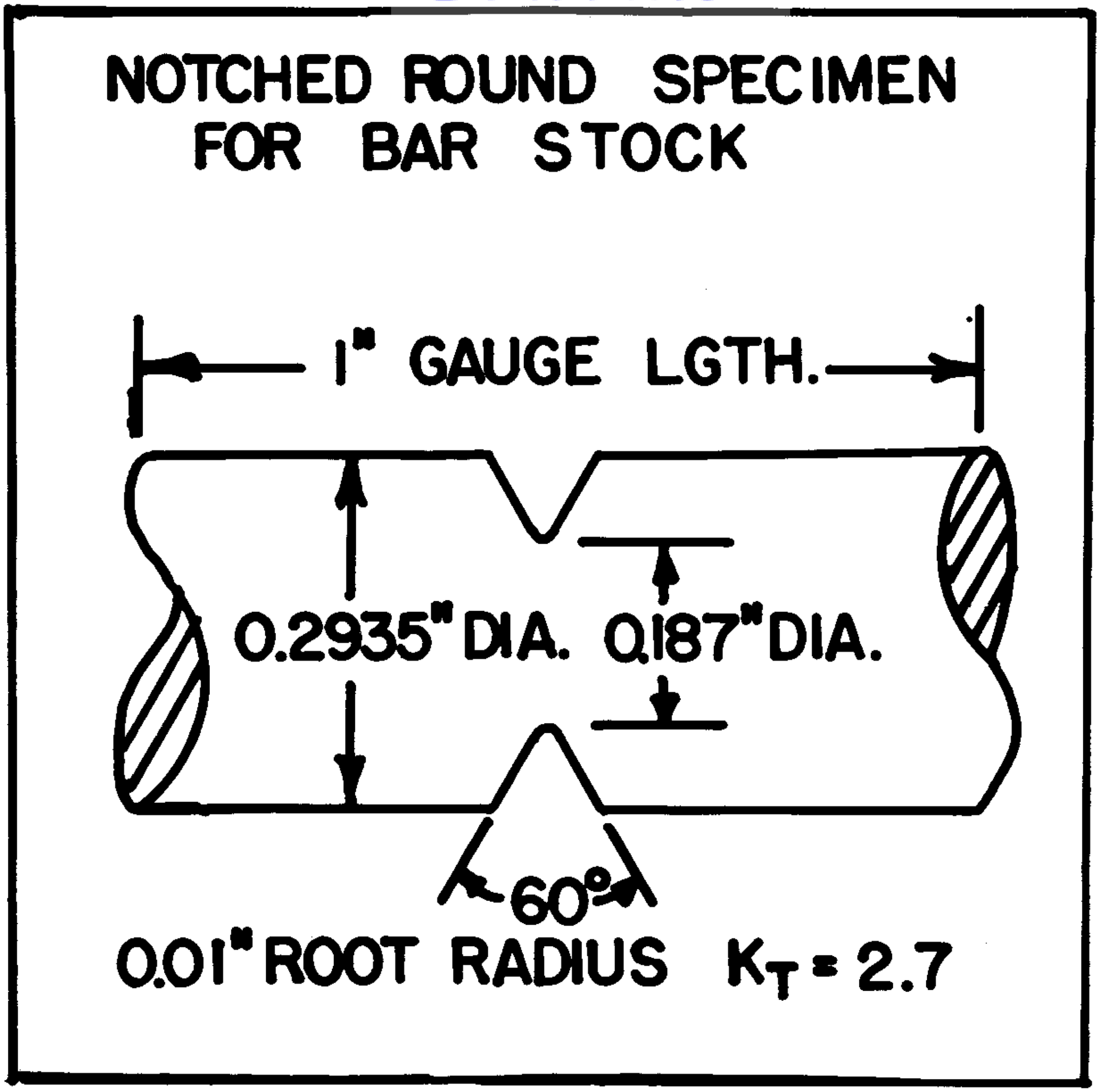


Figure 1

Vee Notched Round Gage Section

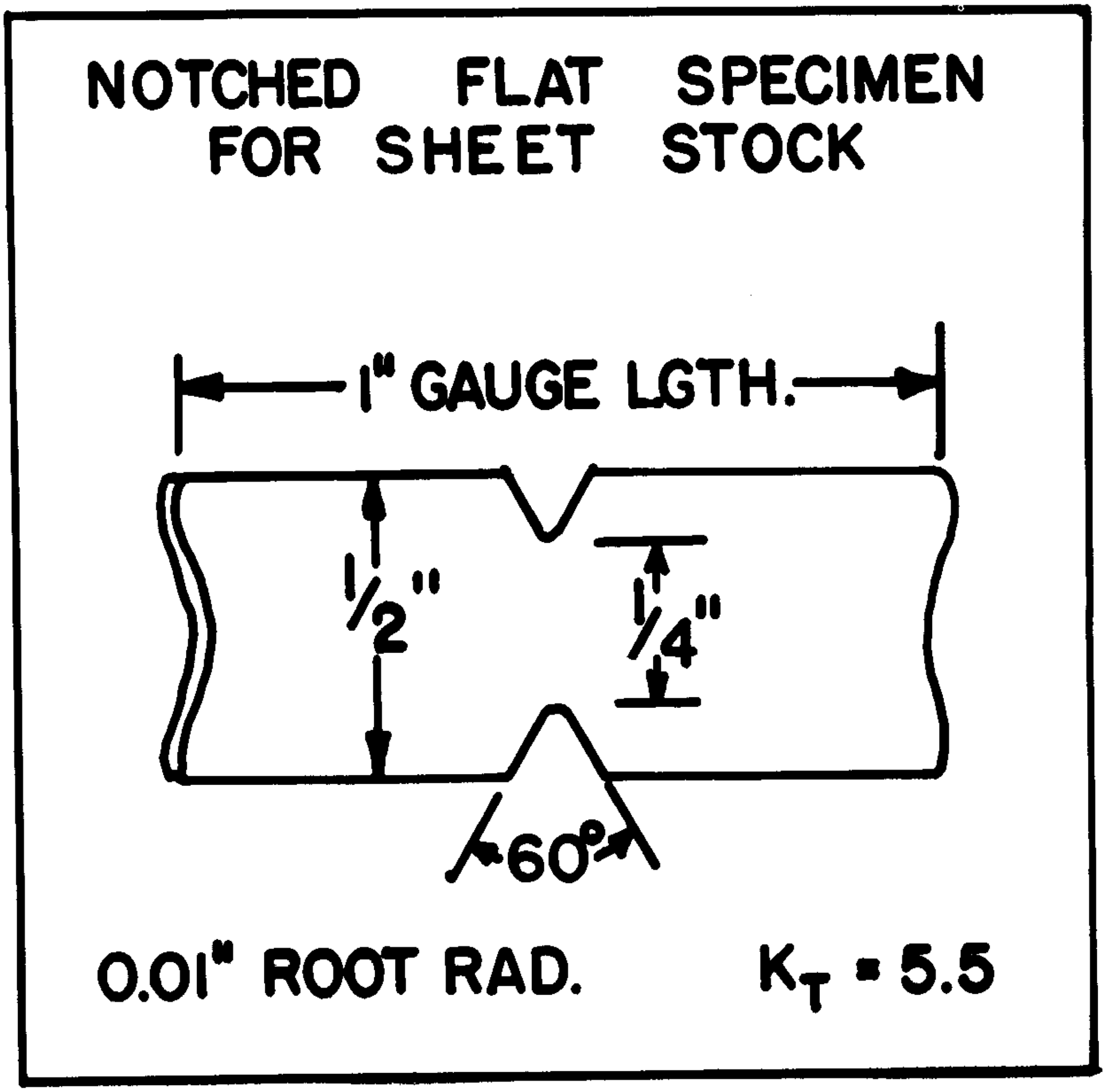


Figure 2

Vee Notched Flat Gage Section

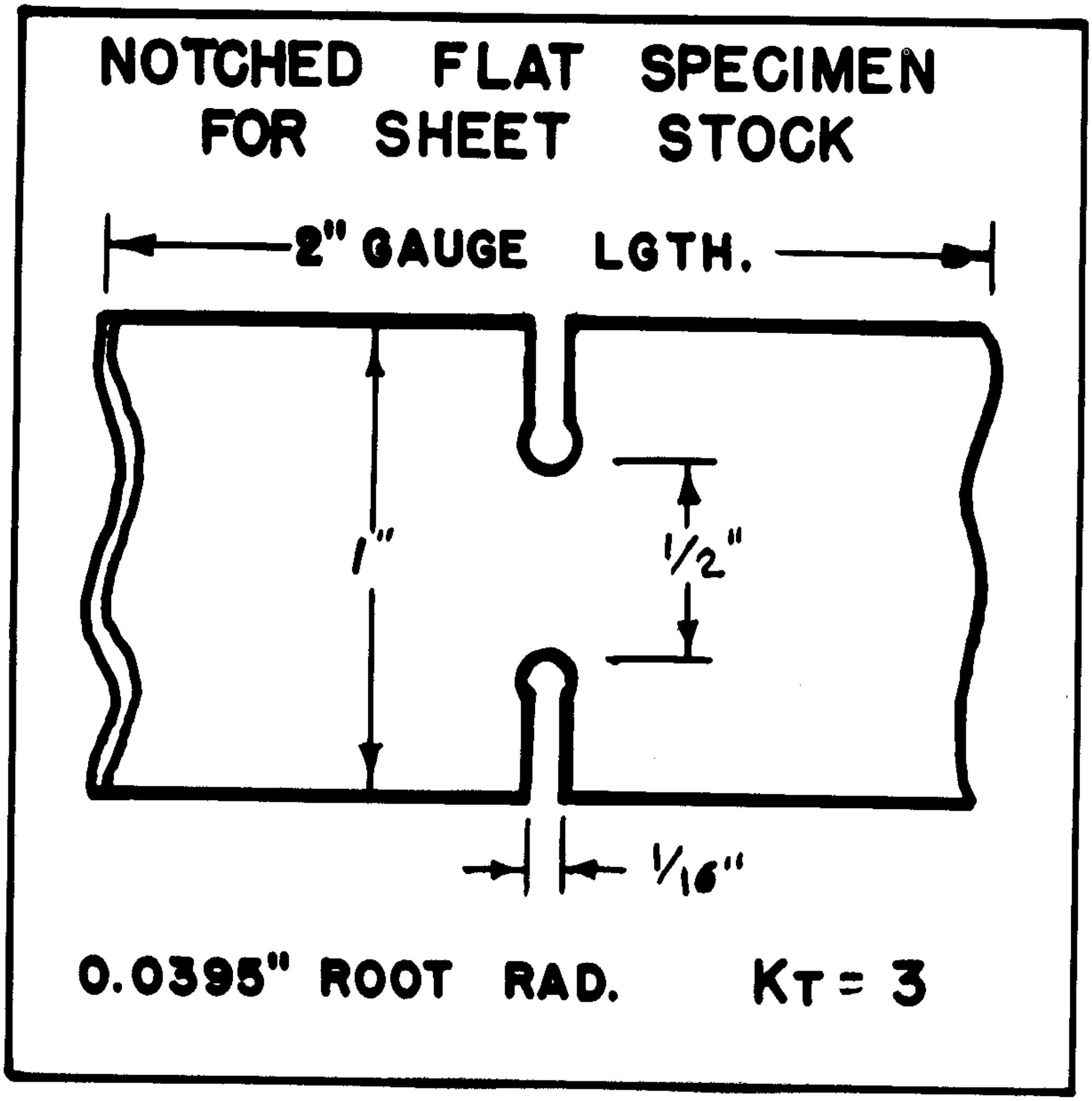


Figure 3

Keyhole Notched Flat Gage Section

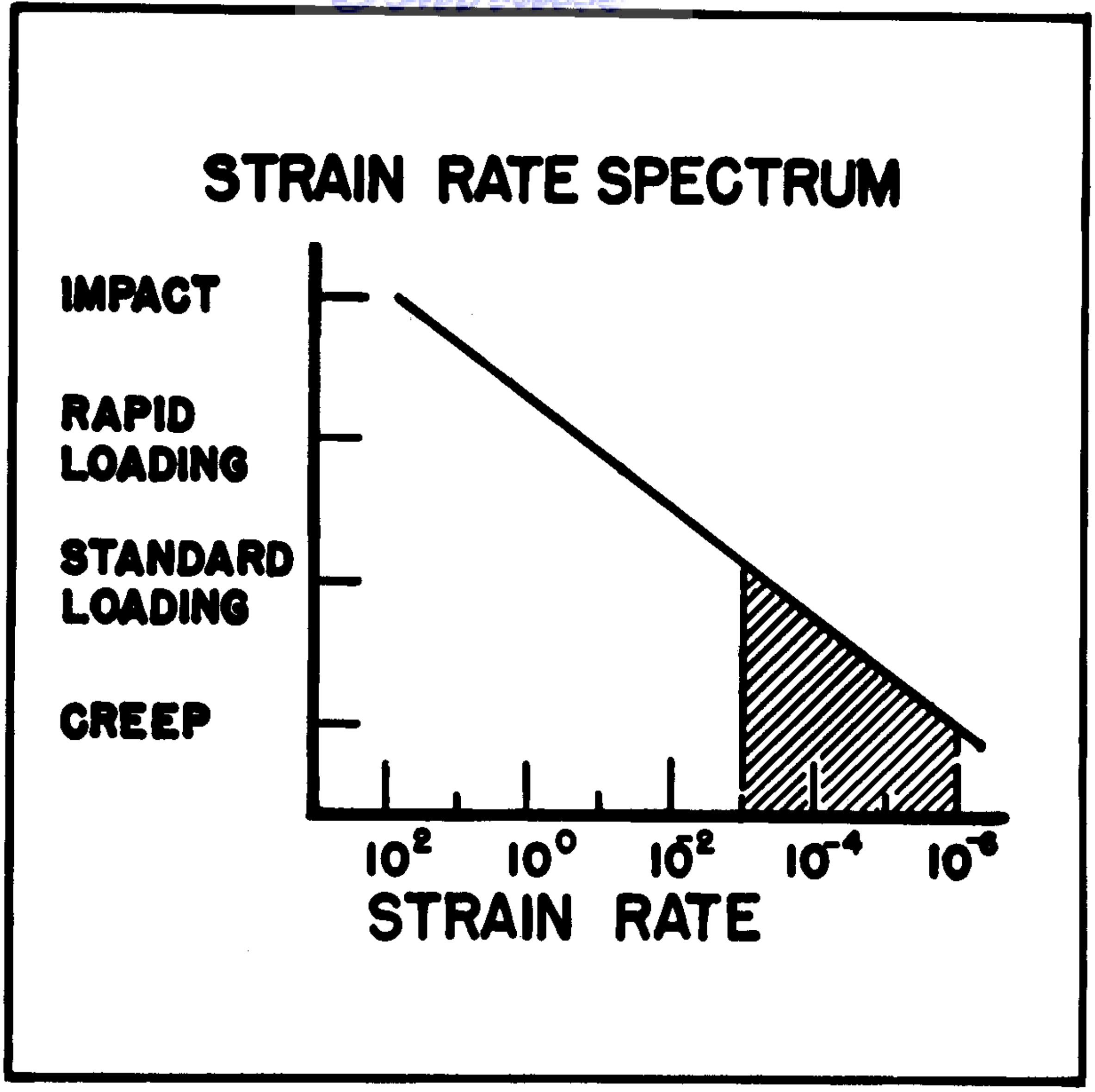


Figure 4

Strain Rate Versus Type of Loading

HYDROGEN EMBRITTLEMENT OF ALPHA-BETA TITANIUM SHEET ALLOYS

by

Lt G. T. Hahn

The characteristics of hydrogen embrittlement of alpha-beta type titanium sheet are essentially the same as described by Lt Burte (see "Hydrogen Embrittlement of Alpha-beta Titanium Alloys," this report). The tensile ductility of sheet specimens contaminated with hydrogen is strain rate sensitive, while specimens subject to sustained loading suffer premature failures. Data presented in this paper illustrate the effect of hydrogen contamination on the mechanical properties of an experimental Ti-140A sheet alloy and on commercial Ti-8% Mn sheet.

HYDROGEN EMBRITTLEMENT OF Ti-140A SHEET ALLOY

Experimental Procedure. The material used in this study, an experimental modification of Ti-140A alloy in the form of 0.064" gage sheet, was submitted for evaluation to the Materials Laboratory, Directorate of Research, Wright Air Development Center, by the Titanium Metals Corporation of America some time before the hydrogen crisis. The chemistry of the alloy, as determined at the Materials Laboratory is shown in Figure 1. Hydrogen analyses conducted at Battelle Memorial Institute on three samples from widely separated points in the sheet indicated hydrogen contents of 374 ppm, 432 ppm, and 513 ppm.

The material was tested in the as-received condition, and after vacuum annealing for 24 hours at 1300°F followed by a furnace cool. The vacuum annealing treatment reduced the hydrogen content to 20 ppm. The effect of the anneal on the microstructure is shown in Figure 2. It appears that some recrystallization, as well as grain coarsening, took place during the anneal. This change is also reflected in the comparison of the standard tensile properties (testing speed: 0.003 to yield, 0.1 in/min from yield to fracture) in Figure 3. In the as-received condition, the material exhibited moderate strength and exceptionally good ductility. The vacuum annealing treatment resulted in a decrease in strength and improved ductility.

Tensile tests were conducted at three different strain rates: 0.1 in/min, 0.02 in/min, and 0.005 in/min at room temperature; and at two rates: 0.02 in/min and 0.005 in/min at -70°F. Room temperature stress-rupture tests of unnotched and notched specimens were conducted on both as-received and vacuum annealed material. Standard size sheet tensile specimens were used for unnotched tensile and stress-rupture tests. The key-hole type specimen (see paper by R. Klinger, "Mechanical Property Test Methods Used For The Evaluation of Hydrogen Embrittlement" for detailed description of specimens and test procedure) was employed for notch stress-rupture tests.

Discussion of Results. The results of the tests, showing the strain rate dependence of the ultimate tensile strength, elongation, and reduction in area, as well as the effect of sustained loading are presented graphically in Figures 4 through 10, and are summarized below:

a. Strain Rate Sensitivity of Ultimate Tensile Strength. The tensile strength values obtained for the as-received material (Figure 4) showed no dependence on strain rate at room temperature, nor at -70°F. This was also the case for the vacuum annealed specimens (data not shown).

b. Strain Rate Sensitivity of Elongation. Elongation values obtained at room temperature for the as-received sheet at the three testing speeds show no dependence on strain rate (Figure 5). At -70°F a slight decrease in elongation was noted with decrease in testing speed from 0.02 in/min to 0.005 in/min.

c. Strain Rate Sensitivity of Reduction in Area(1). For the as-received material (Figure 6) a pronounced decrease in reduction in area was observed at the slowest strain rate, both at room temperature and at -70°F. Reduction in area values for the vacuum annealed material on the other hand (Figure 7) showed absolutely no strain rate sensitivity.

d. Mode of Fracture. The photographs presented in Figures 8 and 9 show the appearance of the fractures typical of the vacuum annealed and as-received tensile specimens tested. Vacuum annealed specimens failed in a ductile manner with considerable necking under all testing conditions. As-received specimens tested at the three testing speeds at room temperature also exhibited ductile fractures. However, at -70°F as-received specimens tested at the slowest strain rate failed in a very brittle manner without perceptible necking. Duplicate specimens tested at this temperature at 0.005 in/min appear to have shattered into three pieces in the course of fracture. It is interesting to note that such brittle fracture was in one case accompanied by 17% elongation.

e. Sustained Loading. Unnotched specimens proved to be unsatisfactory. As-received specimens failed in the grip area in the region of the stress concentration induced by the pinhole.

The results of the notched stress rupture tests are shown in Figure 10. As-received specimens subjected to nominal stresses greater than 50% of the notched ultimate tensile strength failed prematurely. Such premature failures were characterized by the formation of a crack at the root of one or both of the key-hole notches. These cracks slowly penetrated the gage section in the plane of maximum tensile stress, progressively reducing the effective cross-sectional area of the specimen. Failure of the specimens generally occurred 2 to 6 hours after the first signs of a crack had been observed. In that period of time the crack would grow so as to extend 1/8" to 3/16" into the gage section. The appearance of the fracture suggests that the specimens finally break in a ductile manner simply as a result of overloading.

No premature failures were observed for the vacuum annealed specimens tested. A vacuum annealed specimen loaded to 77% of the notched ultimate strength had not failed after 600 hours.

Conclusions. While the results of the tensile tests conducted at the slowest rate of straining, 0.005 in/min(2), do provide some evidence of the strain rate sensitivity characteristic of hydrogen embrittlement, the effect can hardly be classified as pronounced. On the basis of the tensile data there appears to be little or no indication that the as-received material would perform unsatisfactorily in service at room temperature. However, the results of the sustained loading tests conducted at room temperature suggest the opposite view. The premature failures observed at relatively low stresses indicate that material in the as-received condition would not perform satisfactorily in service. If the as-received sheet, for example, were subjected to a slight overload at a rivet hole or other discontinuity in service, a crack could be expected to form at that point in a matter of hours. In the absence of hydrogen, the same sheet would deform locally to permit a readjustment of stresses, and would then, barring further mishaps, last indefinitely.

In the light of data presented by Lt Burte (see "Hydrogen Embrittlement of Alpha-Beta Titanium Alloys," this report), there is little doubt that the difference in behavior of the as-received and vacuum annealed material can be attributed to hydrogen. Perhaps the more significant conclusion that can be drawn from the test results is the inadequacy of tensile data as a means of detecting hydrogen embrittlement.

HYDROGEN EMBRITTLEMENT OF Ti-8% Mn SHEET

In order to determine the effect of heat to heat variations in chemistry and properties on the sensitivity to hydrogen embrittlement, and also to evaluate the sustained loading test as a means of detecting hydrogen embrittlement, a number of different heats of 8% Mn sheet were tested in stress rupture. This work has not been completed. Preliminary results are discussed below.

Experimental Procedure. To simulate possible commercial testing procedure, duplicate specimens from different heats in the as-received condition were tested in stress rupture under a comparative stress level, a given percentage of the notched ultimate tensile strength. A more extensive evaluation was conducted on Heat No. A-3810-B11 to establish an optimum stress level for the sustained loading tests. The chemistry of this heat is shown in Figure 11. Except for the hydrogen content, which is relatively high, the chemistry meets specification requirements. This material was tested both in the as-received condition, and after vacuum annealing for 24 hours at 1200°F followed by a furnace cool. The effect of the annealing treatment on the microstructure is shown in Figure 12, and is similar to that described for Ti-140A.

All tests conducted on 8% Mn sheet employed the sub-size specimens described by R. Klinger, "Mechanical Property Test Methods Used for the Evaluation of Hydrogen Embrittlement," this report. Tensile tests to establish notched and unnotched properties were conducted at the standard testing speed, 0.003 in/min to yield, 0.1 in/min from yield to fracture.

Discussion of Results. A comparison of the tensile properties of as-received and vacuum annealed sheet, Heat No. A-3810-B11 (discussed above), is shown in Figure 13. The properties of the as-received material are well within the producers specifications. The effect of the annealing treatment on the tensile properties, lower strength and improved ductility, is again similar to that reported for the Ti-140A sheet.

The results of the sustained loading tests on this same heat are shown graphically in Figure 14. As-received specimens loaded to more than 50% of the notched ultimate tensile strength failed prematurely, while vacuum annealed specimens loaded to as much as 80% of the notched ultimate strength had not failed after much longer periods of time. Fracture of as-received specimens was preceded by the same sequence of events previously outlined for the as-received Ti-140A material. The premature failure of as-received material at comparatively low stresses is indicative of hydrogen embrittlement. It is interesting to note that the stress-rupture characteristics of the 8% Mn sheet (Figure 14) and the Ti-140A sheet (Figure 10) are very similar, although different types of notched specimens were used in the evaluations. It would therefore appear that the configuration of the notch is not critical in this type of test.

On the basis of the results obtained for Heat No. A-3810-B11, specimens of the remaining heats were subjected to 80% of the notched ultimate tensile strength. It was felt that at this stress level material not contaminated with hydrogen would last indefinitely. The results to date of stress-rupture tests conducted on heats of 8% Mn sheet are shown in Figure 15. The heat designations tabulated refer to a Materials Laboratory coding system. Heat designation DG corresponds to Heat No. A-3810-B11.

With the exception of the specimen of Heat DL, which appeared to have failed in the ductile manner, specimens of the remaining heats exhibited the characteristic crack induced fracture of hydrogen embrittled material. This fact, and the relatively long period required for fracture suggests that DL failed normally and not as a result of hydrogen embrittlement. Premature fracture of the remaining heats is attributed to hydrogen contamination.

Where duplicate specimens were tested, the results obtained appear to be fairly reproducible. For this reason it is rather doubtful that the difference in time to fracture for heats AB and CD can be attributed to scatter. Therefore, if time to fracture is a sensitive indication of the severity of the embrittlement, then there appears to be no correlation between hydrogen content and the severity of the embrittlement among the heats which failed prematurely. It should be noted that this conclusion presupposes that stress-rupture tests conducted at a constant percentage of the notched ultimate tensile strength produce the same tendency for premature fracture in different materials; and that variance in time to fracture can then be attributed to factors other than the severity of the test. Provided that such a view is acceptable as a first approximation, the results indicate that other factors such as heat to heat variations in chemistry, thermal history, and structure influence the sensitivity of an alloy to hydrogen embrittlement.

The data presented are far too fragmentary to deliniate a hydrogen tolerance for the 8% Mn alloy, but merely illustrate some of the problems that may be encountered in stress-rupture testing of sheet.

GENERAL CONCLUSIONS

1. The effects of hydrogen contamination on the properties of alpha-beta type titanium sheet alloys are essentially the same as previously described for bar and forging stock. Hydrogen embrittlement is characterized by premature failure under conditions of sustained loading, and loss in tensile ductility with decreased speed of testing.

2. The tensile properties of sheet, particularly ultimate tensile strength and elongation, appear to be relatively insensitive to speed of testing. Loss in ductility as measured by reduction in area values provides the most sensitive indication of hydrogen embrittlement. Results obtained for Ti-140A indicate that unless extremely slow rates of straining are used the tensile test will fail to provide evidence for serious loss in strength in sustained loading.

3. Notched stress rupture specimens appear to be more sensitive to hydrogen embrittlement than unnotched specimens. Notched specimens of as-received Ti-140A experimental sheet with 440 ppm hydrogen, and one heat of commercial 8% Mn sheet with 260 ppm failed prematurely when subjected to sustained loads greater than 50% of the notched ultimate tensile strength. It should be noted, however, that the use of hydrogen contaminated sheet in critical applications, even where the design stress is lower than the stress required for premature failure in stress-rupture, is not justified. There is rarely a guarantee that the design stress will not be exceeded some time in service.

4. Preliminary results of a study dealing with different heats of Ti-8% Mn sheet suggested that factors other than hydrogen content, such as heat to heat variation in chemistry, thermal history, or microstructure, may influence the sensitivity of an alloy to hydrogen embrittlement.

---

(1) Whereas the reduction in area of sheet specimens is generally not measured, previous experience with bar stock suggested that in some cases reduction in area values were more sensitive to hydrogen embrittling effects than corresponding elongation values. Minimum width and thickness values at the necked portion were measured with a screw thread comparator (pointed anvil micrometer) and averaged to obtain reduction in area values. Values so obtained were in general more reproducible than elongation values.

(2) It should be noted that this test requires more than one hour to complete, and may be generally impractical for this reason.

DISCUSSION

Parris: I have some data that illustrate an instance where hydrogen embrittlement in sheet is shown by the tensile test. The data were obtained during an evaluation of the properties of 3 Mn Complex sheet from a single heat of the alloy. The sheet was all rolled at the same time at 1450°F. Both the alloy and the heat treatment used were different from those discussed by Lt Hahn, and this might explain the difference in behavior. The difference in hydrogen contents was occasioned by the different methods of pickling used.

The results are shown on this slide (reproduced as Figure 16). The ductility as measured by elongation is plotted against tensile strength across the bottom. The sheet which contained 100 PPM of hydrogen, even at the very high strength levels of 180,000 psi, had excellent ductility. The testing speed used was relatively slow, 0.02 in/min. However, with 200 ppm of hydrogen the ductility dropped off very sharply. We have only one point at a very high hydrogen level, 600 ppm, and that showed essentially zero ductility. As you can see, the ductility at low strength levels was still relatively high with 200 ppm.

This just illustrates a point which Lt Hahn made, and Lt Burte before him; that there are a great many factors about this hydrogen embrittlement which we do not understand as yet, such as the manner in which interstitials, heat treatment, and fabrication variables affect hydrogen embrittlement.

Sachs: In the study of possible test methods for hydrogen embrittlement of steel we are coming more and more to the conclusion that the bend test on the unnotched specimen will be the ultimate solution. I have specific types of bend tests in mind which approach the constant rate test, and which allow testing at the extremely low strain rates. Now we have found that constant strain rate tests and such rupture tests do rate the material, in general, parallel. The bend tests do have two very definite advantages. The preparation of specimens for bend testing is considerably less expensive than any other type of tensile specimen. In addition it is possible to build a relatively inexpensive machine which can take a considerable number of test specimens, automatically break them, and record the results of the tests. This is very important since we need a large number of specimens for an evaluation of hydrogen embrittlement at the present state of knowledge. And that is quite a thing for me to admit, since I've been so strong for the notch test.

I don't think that the notch test should be used for hydrogen embrittlement for the simple reason that we have a very complex phenomenon in hydrogen embrittlement, and the notch test is a very complex type of test. It only rates relatively low ductilities. The notch test doesn't mean a thing for high ductility materials.

Kotfila: That was a very interesting comment Dr. Sachs, and I will agree with you that we have overlooked a lot of things. I believe that the people in our mechanical testing section are going to look into the methods and type of tests that will show this embrittlement the best. The reason we adopted the stress rupture test was because of past experience with it. We did not have time to evaluate all the types of tests that were available. Did you confine your remarks strictly to sheet?

Sachs: We are actually testing very large forgings to some extent and we feel that the preparation of small flat specimens out of the forgings will be a very inexpensive affair. The notched stress-rupture tests are not only very difficult to interpret, but as far as slow rates are concerned, it is almost impossible to provide the necessary number of stress rupture machines to run any reasonable number of tests.

Kotfila: Are your findings published, or are they in the process of being evaluated?

Sachs: The first results will be submitted to the Wright Air Development Center within a short time. They refer to the high strength steels which are in the foreground of interest for landing gear applications. We have a little parallel study which is more of a fundamental character for Watertown Arsenal on the way, and I am not sure when progress reports will be available.

Hahn: In connection with Dr. Sachs' remarks I want to discuss our experience on the usefulness of the bend test as a means of detecting hydrogen embrittlement in sheet. We conducted a number of variations of the guided bend test on the Ti-140A sheet I reported on. This material was subject to hydrogen embrittlement in the as-received condition, but was very ductile for fast rates of testing.

First, we conducted guided bends to 180° rapidly so as to complete the bend in 10 minutes, and also very slowly so that the bend operation took over an hour. We found that this difference in testing speed had no effect on the minimum bend radius. Next we conducted what we referred to as "delayed bend tests". This involved bending specimens over a mandrel 60° at a time and letting the specimens age several weeks at room temperature between the bend operations. This also did not appear to effect the minimum bend radius of hydrogen contaminated sheet. Finally, we conducted a type of bend and age under stress test. Specimens were bent to 180° and then placed in jigs to constrain spring-back from 180°. it was thought that this type of test might be analogous to the stress rupture test, and that possible cracks would develop. However, no visible cracks have been observed after as much as 2 months. None of the bend tests conducted on this sheet to date have been successful in detecting hydrogen embrittlement.

Sachs: If I understand your tests correctly, Lt Hahn, you have only one radius. Is that correct?

Hahn: Yes. These tests were conducted using the minimum bend radius that could be induced.

Sachs: That is a constant rate test when you stick to one radius. What I have in mind are tests where you have to work with a constant bending moment, and gradually increase your strain, in other words, reduce your radius. This happens automatically under constant moment.

Anonymous: Did the stress concentration have an effect on the results of the rupture tests?

Hahn: We tested the Ti-140A sheet unnotched, with a keyhole type notch, $K_t=3$, and also conducted tests with subsize specimens with $K_t=4$. The stress rupture characteristics of the hydrogen contaminated sheet was essentially the same for the 2 different notches. However, the unnotched specimens did not break in short periods of time, and not at the minimum section. The specimens finally failed after about 200 hours at the pin holes that supported the specimens in the frame. This would suggest that hydrogen embrittled material is notch sensitive, and that the stress concentration can effect the time for failure in the rupture test.

I prefer to look at this another way. Hydrogen contaminated material embrittles where there is a high localized deformation, and this is presented in the vicinity of the notch. The specimen will fail prematurely provided you have sufficient deformation at the root of the notch.

Minkler: One thing we have found in our work is that there are variables in processing other than hydrogen which complicate correlating the results of bend tests or manipulation tests with hydrogen content. There can be a difference in such variables in processing from sheet to sheet in any one heat that will affect the results of a manipulation test.

Have you done any work at all on commercially pure titanium with respect to the effect of hydrogen, that is, on the all alpha composition?

Hahn: No. This subject has been dealt with very carefully by Dr. Jaffee and his associates at Battelle Memorial Institute, and the results have been published.

Durfee: Going along with Dr. Sachs simplification of tests for hydrogen embrittlement, I have tried to prepare a "U" shaped specimen with a strain gage load cell actually in a bolt, and got good correlation. We are continuing this work.

Hahn: I want to add something to the answer to Mr. Minkler's question. It is important to recognize that the hydrogen embrittlement in the alpha material is entirely different from that in the alpha-beta material. The testing procedures which will have to be used in detecting hydrogen embrittlement will have to be correspondingly different.

Ti-140 A (EXPERIMENTAL SHEET)

GAGE: .064 IN.

NOMINAL COMPOSITION:

Ti - 2% Fe Cr - 2% Fe Mo

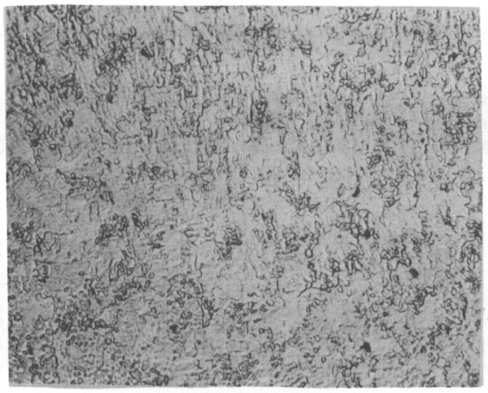
ANALYSIS:

C	0.12 %	N	0.07%
Fe	1.22 %	Cr	1.76 %
Mo	1.19 %		

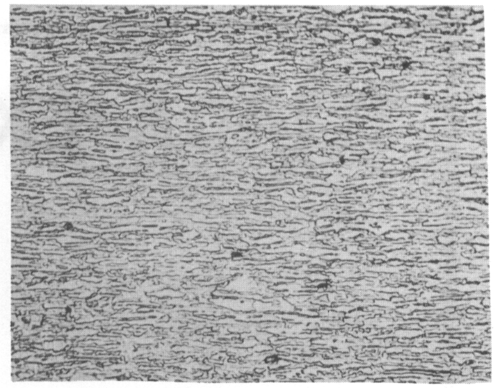
H_2 440 PPM (AVG)

Figure 1

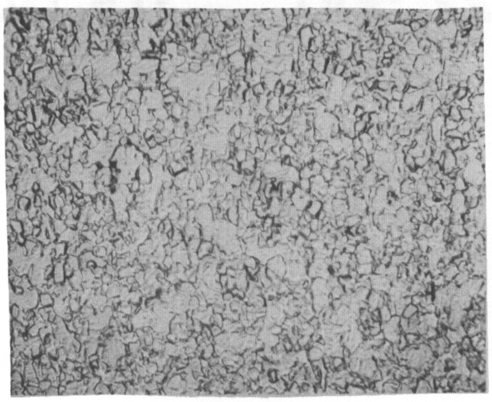
Composition of Ti-140A Experimental Sheet Alloy



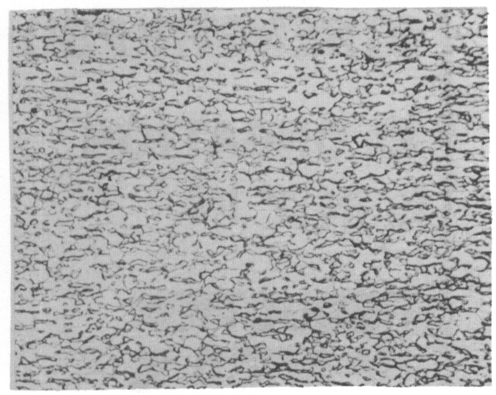
a. As-received, plane of rolling.



b. As-received, longitudinal edge.



c. Vacuum annealed, plane of rolling.



d. Vacuum annealed, longitudinal edge.

Figure 2

Ti-140A Experimental Sheet. Magnification: 500x.
Etchant: 10cc conc. HNO_3, 2cc conc. HF, 88cc H_2O.

Ti 140A EXPERIMENTAL SHEET

	AS RECEIVED	VACUUM ANNEALED
0.2% OFFSET YIELD STRENGTH (PSI)	105,000	103,500
ULTIMATE STRENGTH(PSI)	127,500	113,000
ELONGATION % IN 2 IN.	20	25
REDUCTION IN AREA %	45	53

STRAIN RATE: 0.1 IN/MIN.

Figure 3

Room Temperature Tensile Properties of As-Received and Vacuum Annealed Ti-140A Experimental Sheet

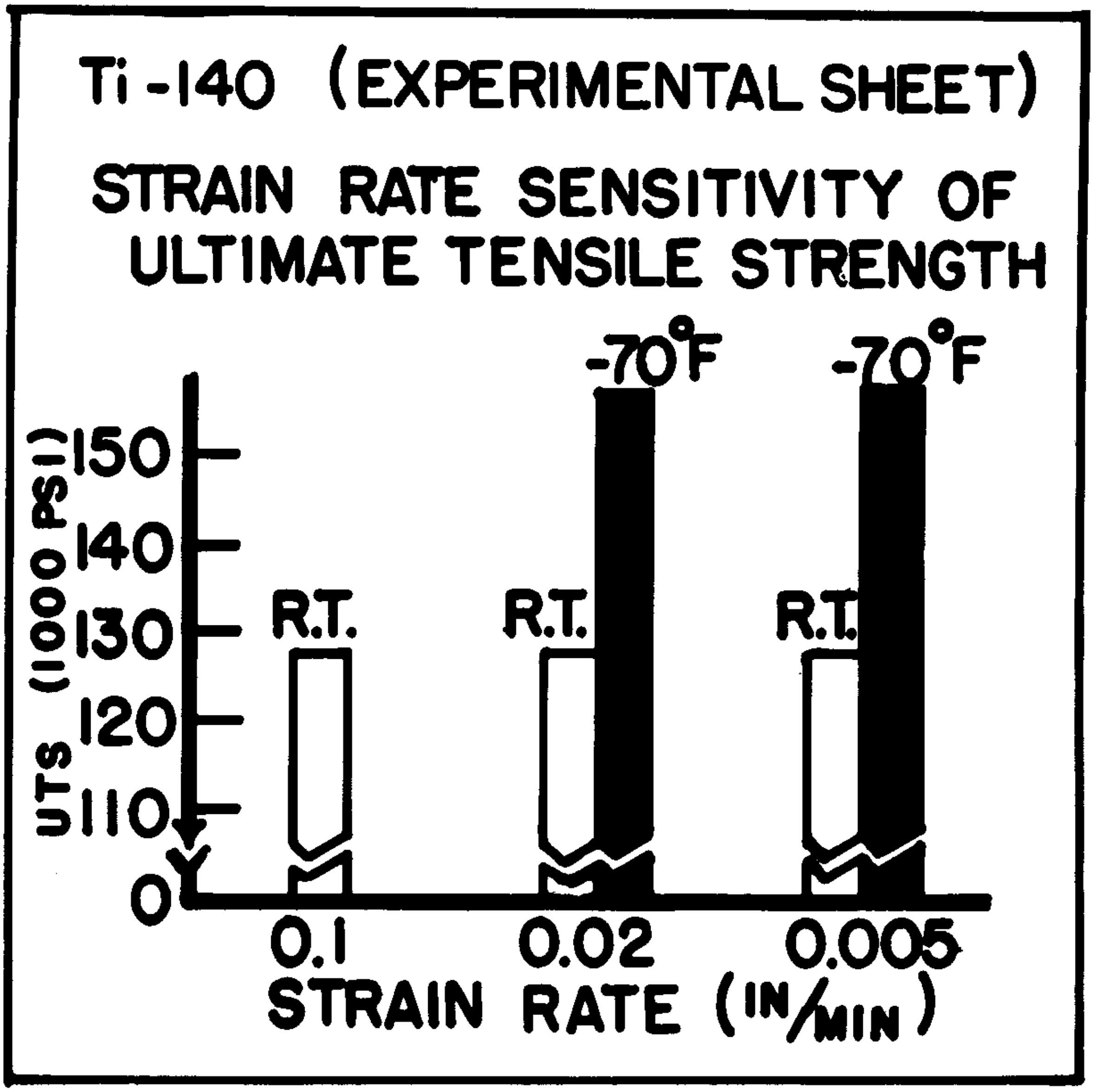


Figure 4

Strain Rate Sensitivity of The Ultimate Tensile Strength of As-Received Ti-140A Experimental Sheet

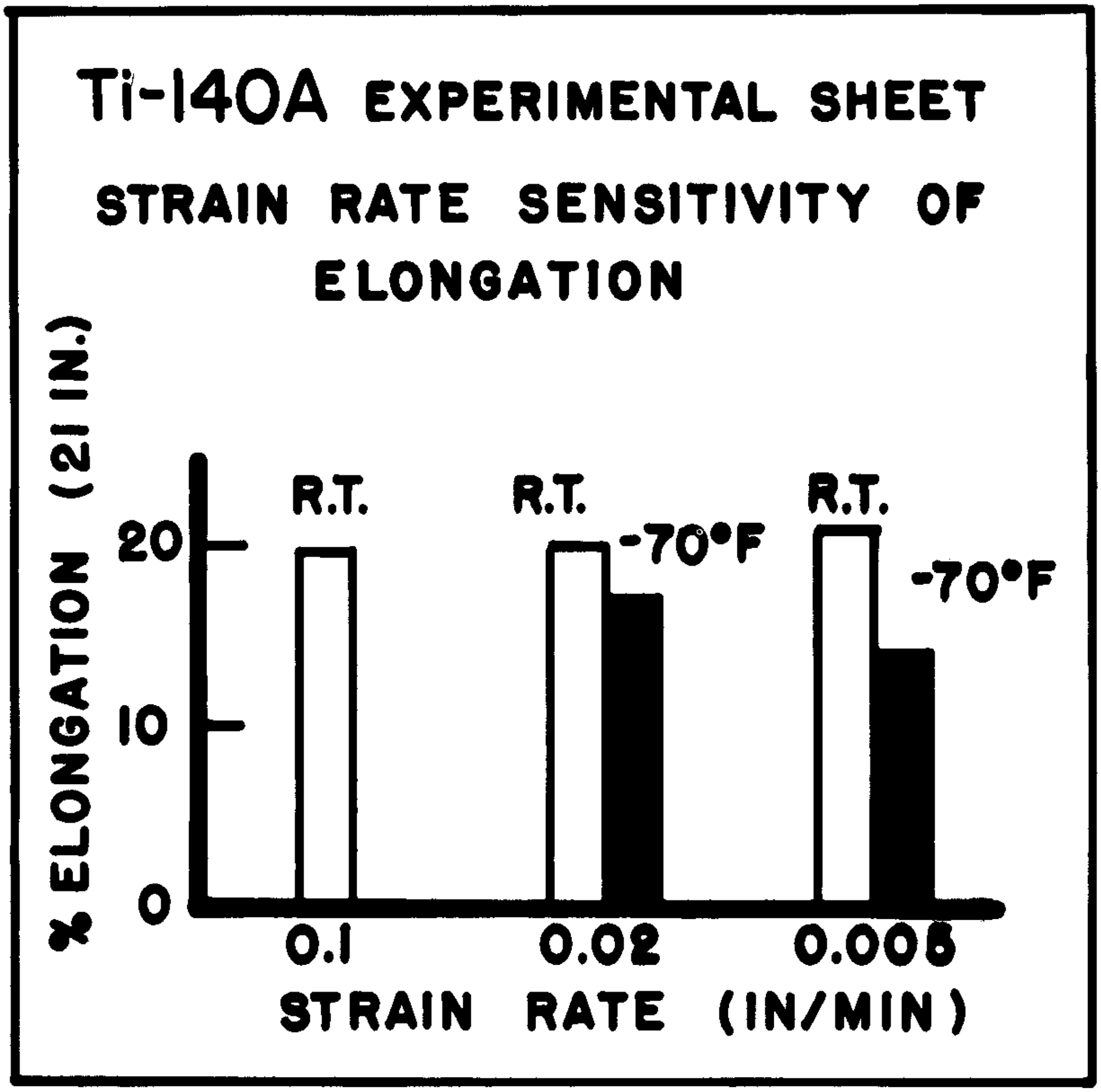


Figure 5

Strain Rate Sensitivity of Elongation of
As-Received Ti-140A Experimental Sheet

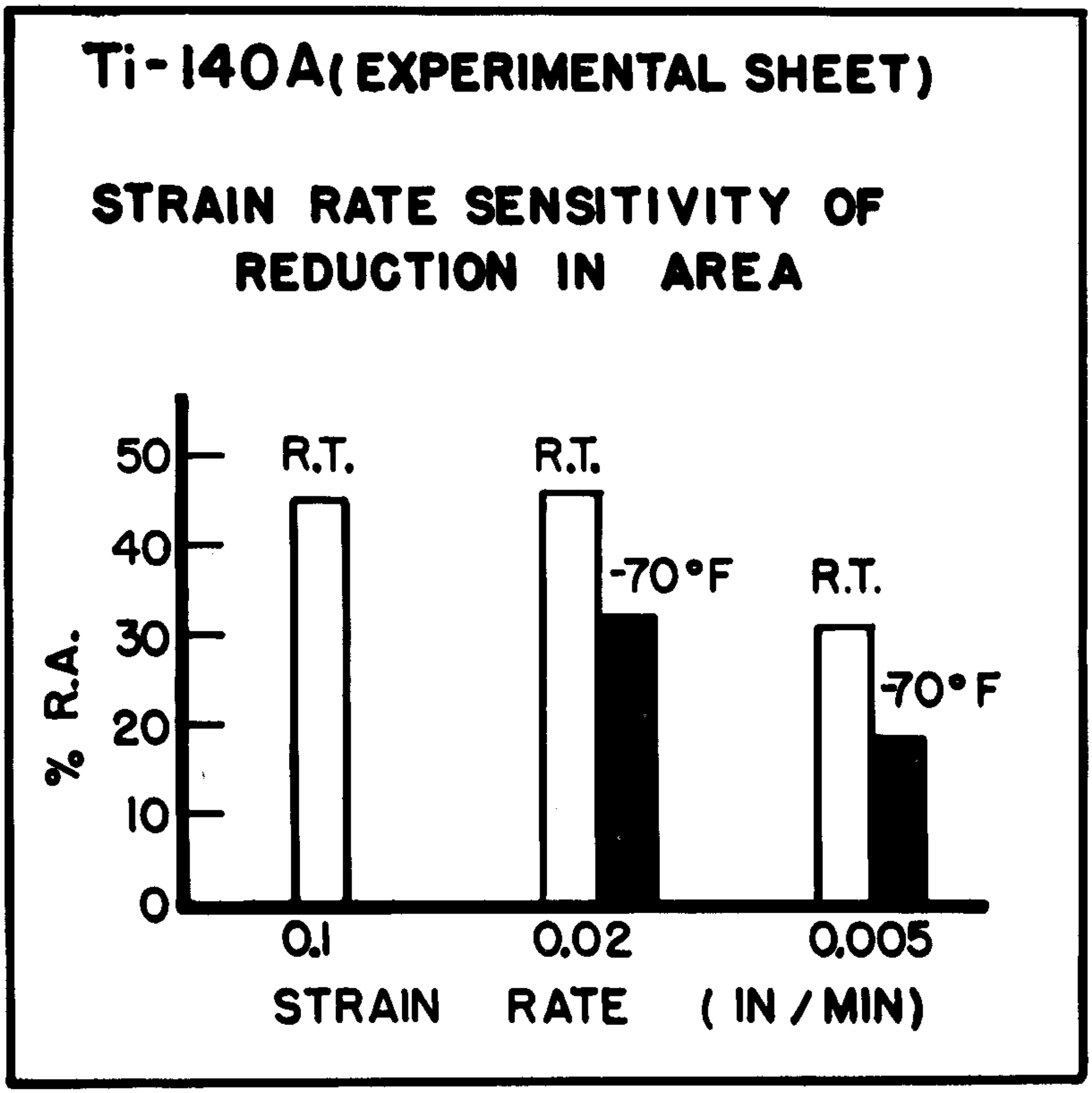


Figure 6

Strain Rate Sensitivity of Reduction in
Area of As-Received Ti-140A Experimental Sheet

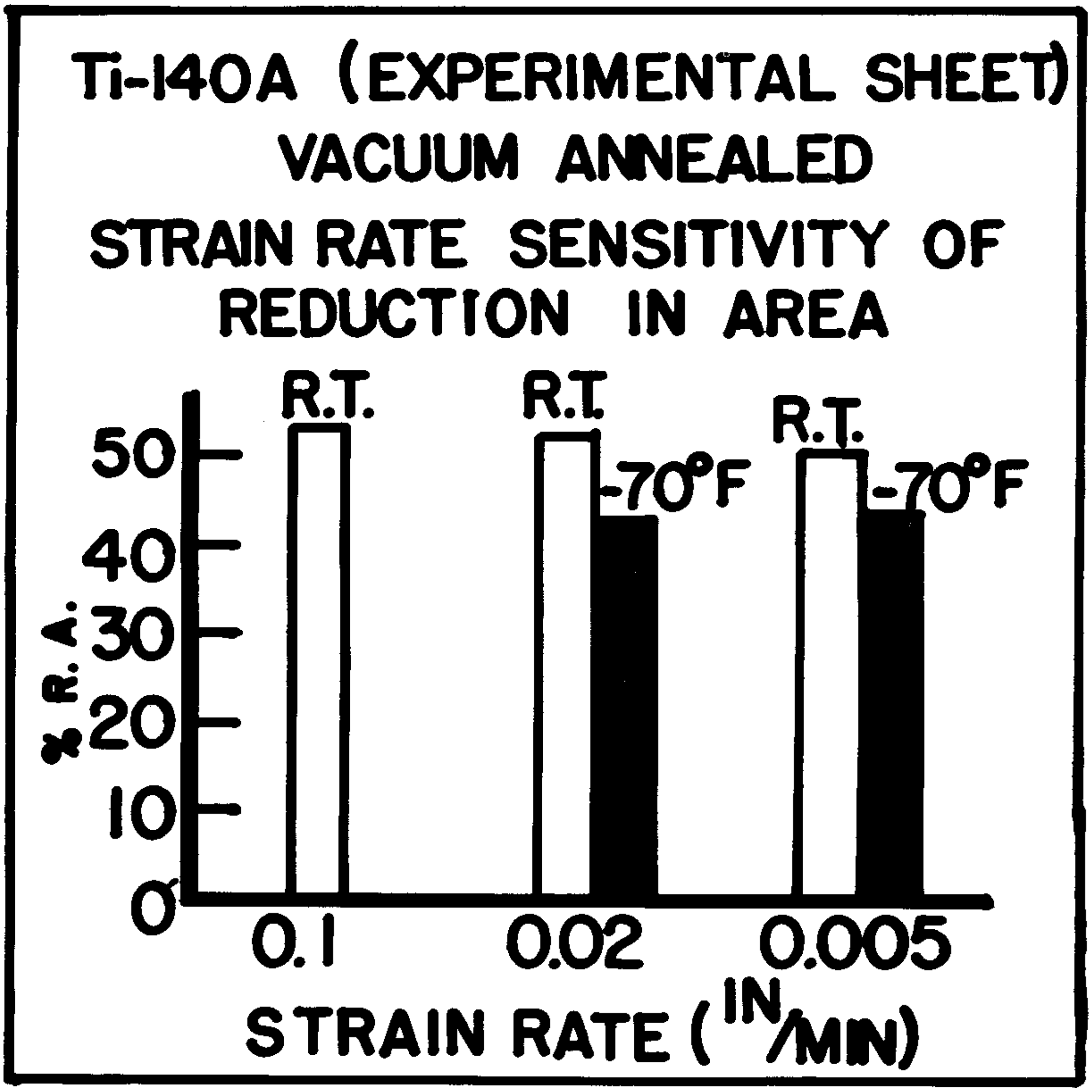


Figure 7

Strain Rate Sensitivity of Reduction in Area of Vacuum Annealed Ti-140A Experimental Sheet

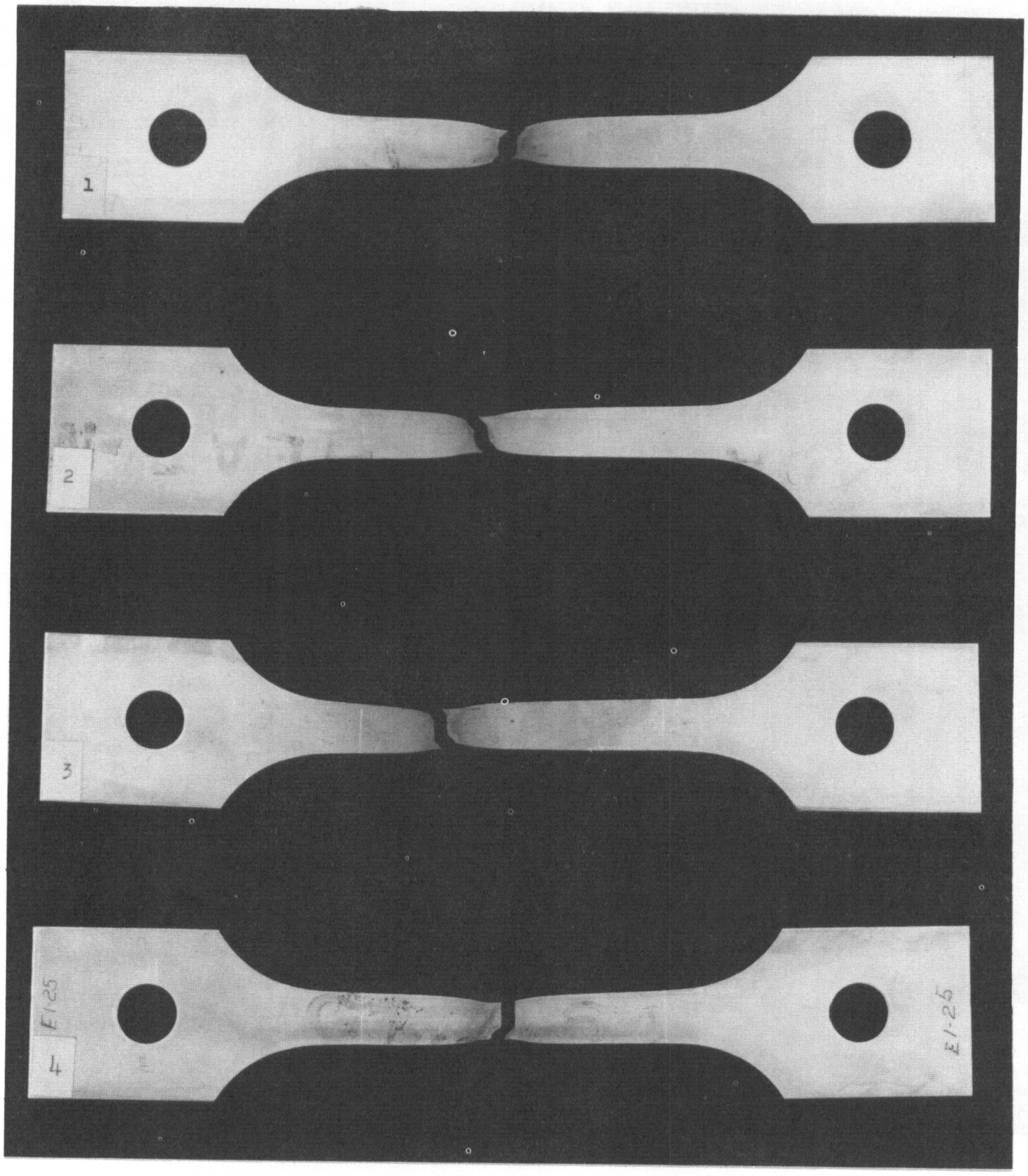


Figure 8

EFFECT OF TESTING SPEED AND TESTING TEMPERATURE ON THE MODE OF FRACTURE OF Ti-140A SHEET IN THE VACUUM ANNEALED CONDITION (20 PPM H_2)

1.	0.1	in/min, Room Temperature;	24% El, 54% RA.
2.	0.02	in/min, Room Temperature;	29% El, 51% RA.
3.	0.02	in/min, -70°F;	27% El, 45% RA.
4.	0.005	in/min, -70°F;	27% El, 45% RA.

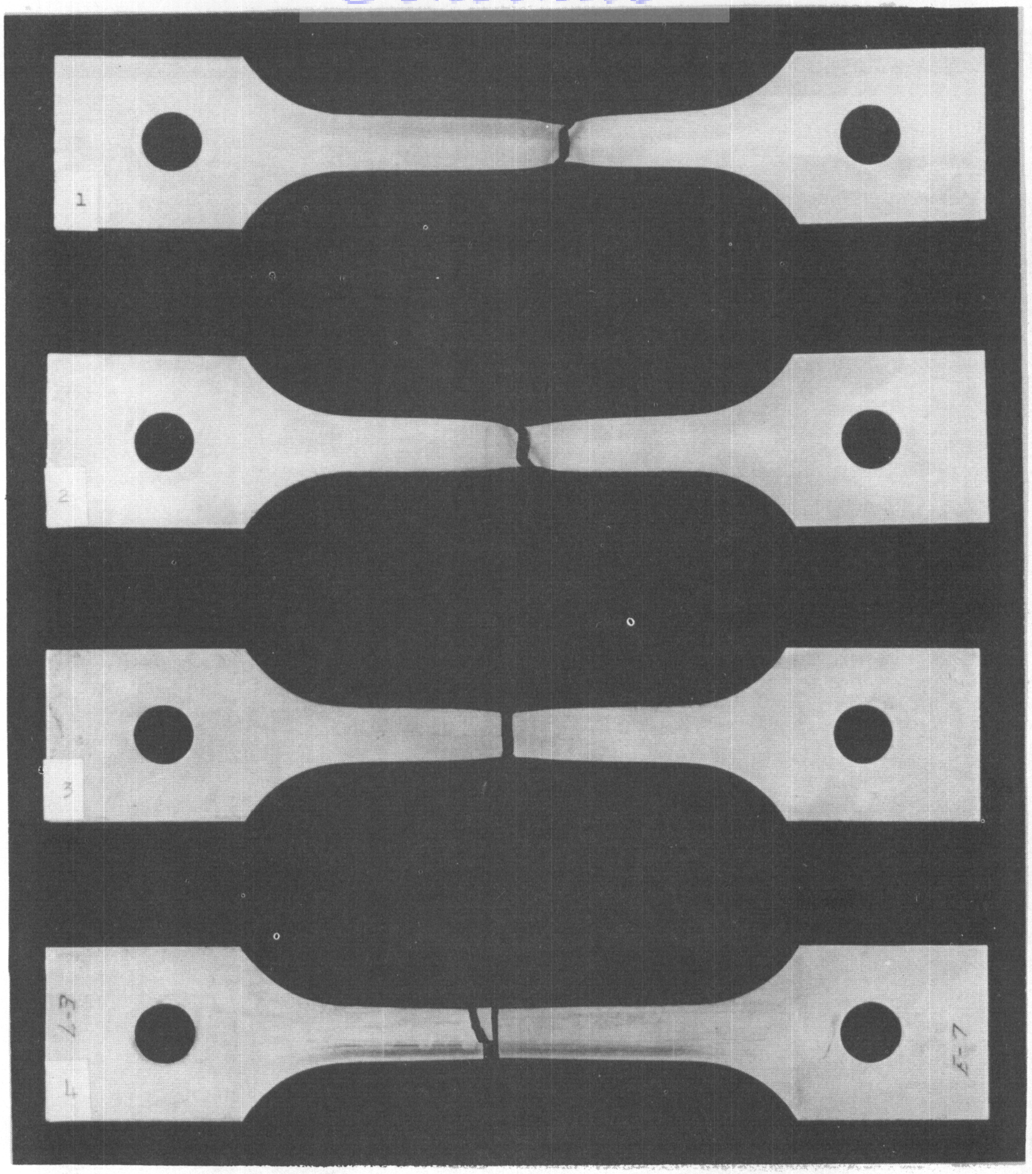


Fig. 9

EFFECT OF TESTING SPEED AND TESTING TEMPERATURE ON THE MODE OF FRACTURE OF Ti-140 A SHEET IN THE AS-RECEIVED CONDITION (440 PPM H_2)

1.	0.1	in/min,	Room Temperature;	19% El,	45% RA.
2.	0.02	in/min,	Room Temperature;	21% El,	46% RA.
3.	0.02	in/min,	-70°F;	16% El,	33% RA.
4.	0.005	in/min,	-70°F;	11% El,	16% RA.

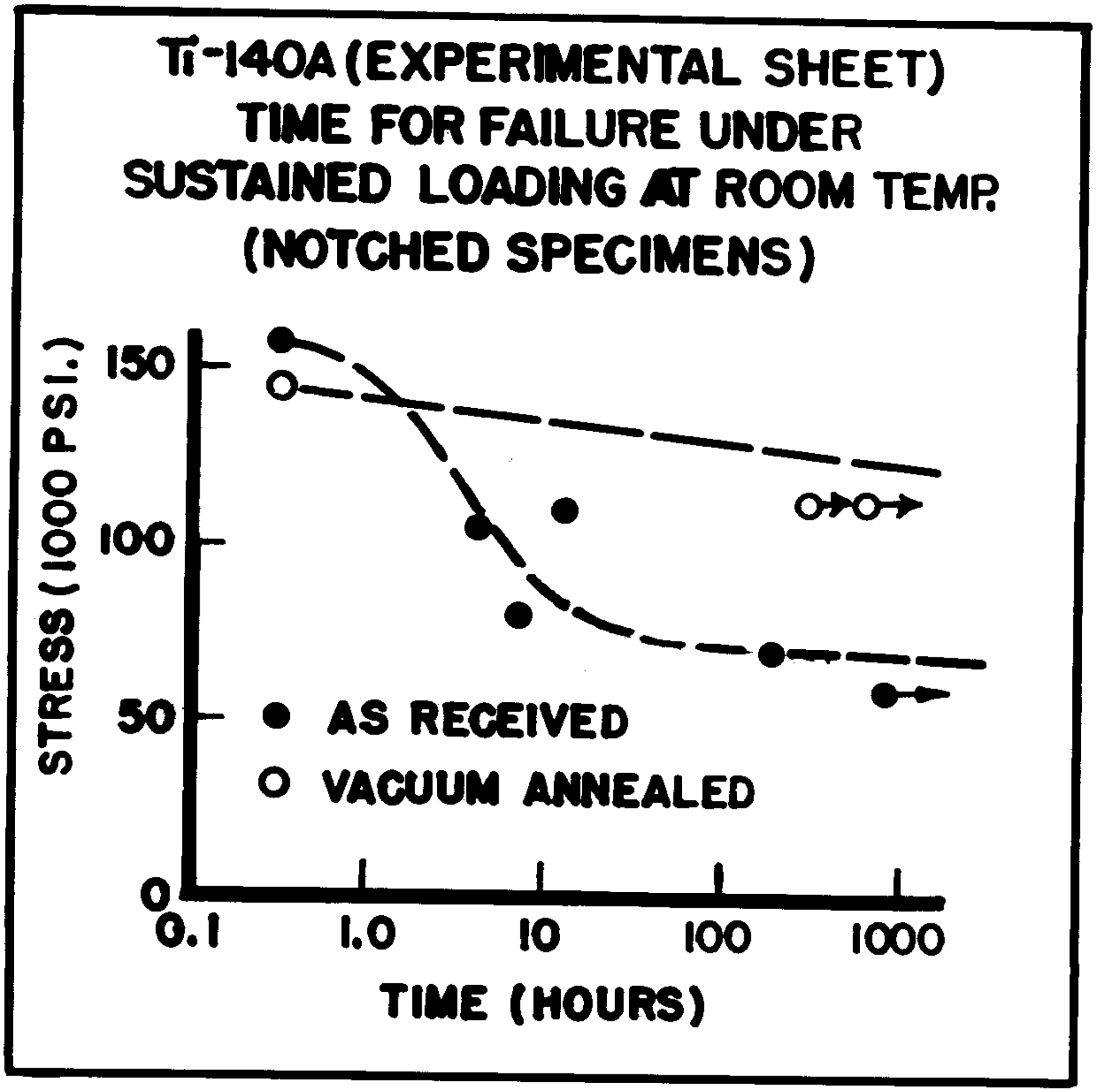


Figure 10

Notched Stress-Rupture Characteristics of
As-Received Ti-140A Experimental Sheet

RC 130A HEAT A3810-B11

GAGE: .051 IN.

NOMINAL COMPOSITION:

Ti – 8% Mn

ANALYSIS:

C	0.08%	Fe	0.14%
N	0.03%	Mn	7.4 %

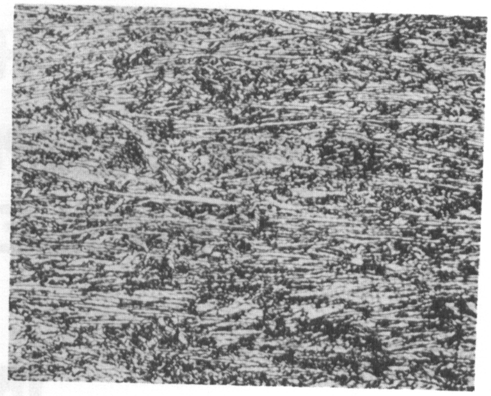
H_2 – 365 PPM

DG

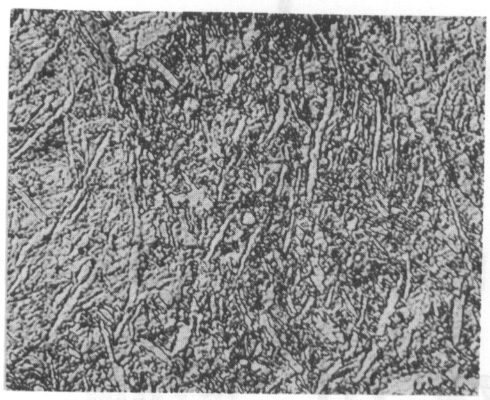
Figure 11

Composition of Commercial Ti-8% Mn Sheet,
Heat No. A3810-B11

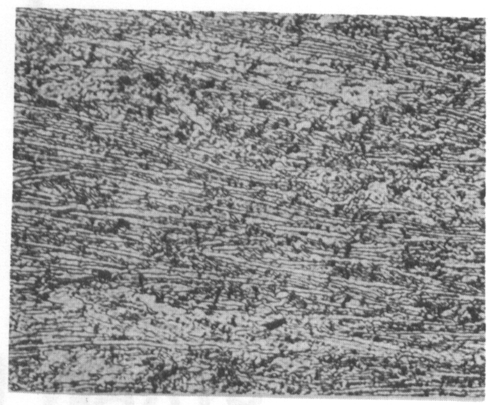
a. As-received, plane of rolling.



b. As-received, longitudinal edge.



c. Vacuum annealed, plane of rolling.



d. Vacuum annealed, longitudinal edge.

Figure 12

RC-130A, Heat A 3810-B11. Magnification: 200x. Etchant: 10 cc conc. HNO_3, 2 cc conc. HF, 88 cc H_2O.

RC 130 A HEAT A 3810-B 11

ROOM TEMPERATURE TENSILE PROPERTIES

	AS RECEIVED	VACUUM ANNEALED
0.2% OFFSET YIELD STRENGTH (PSI)	129,000	126,400
ULTIMATE STRENGTH (PSI)	144,100	132,800
ELONGATION % IN 1.0 IN.	18	23

STRAIN RATE: 0.1 IN/MIN

Figure 13

Room Temperature Tensile Properties of As-Received and Vacuum Annealed Ti-8% Mn Sheet, Heat No. A3810-B11

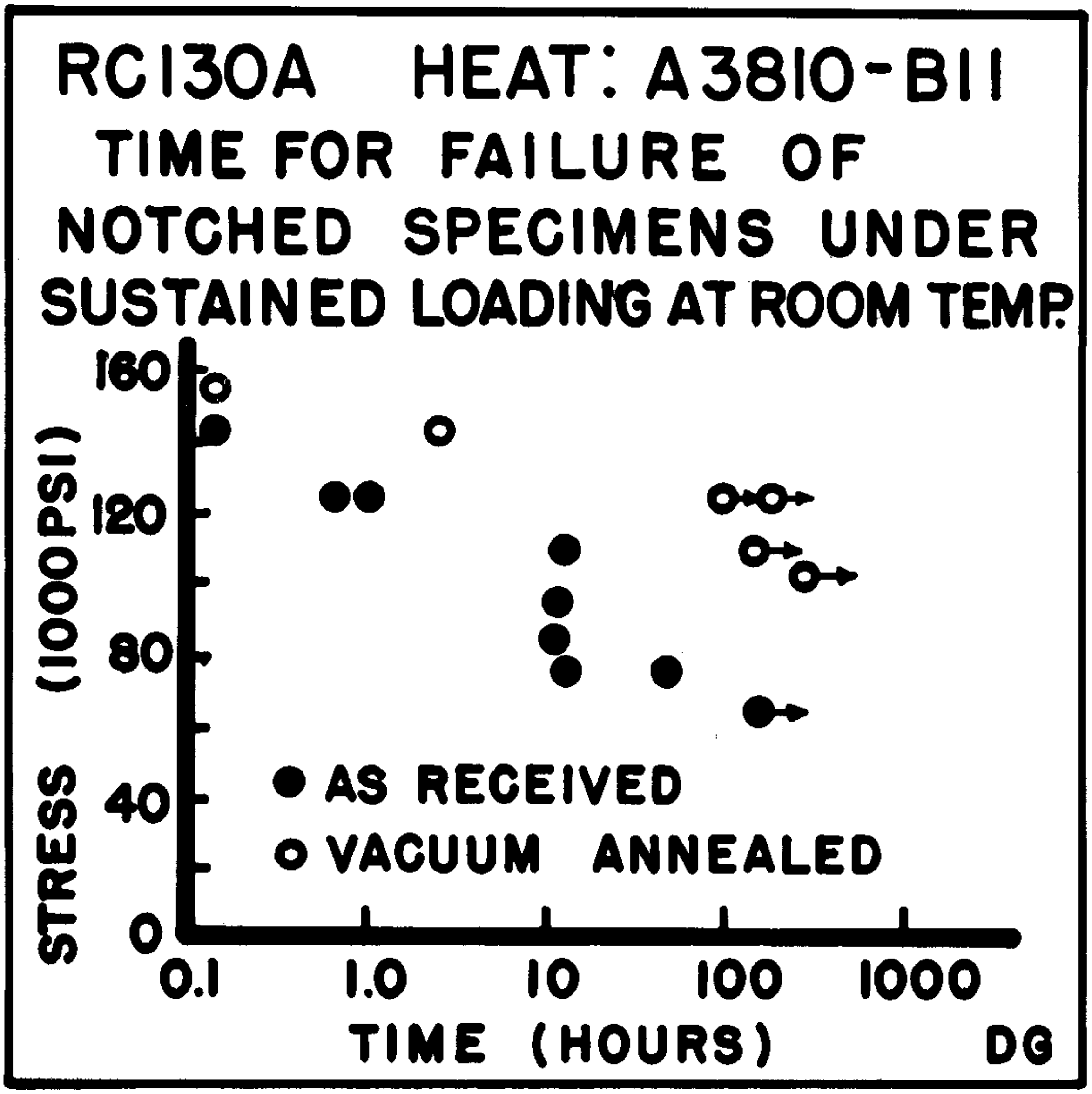


Figure 14

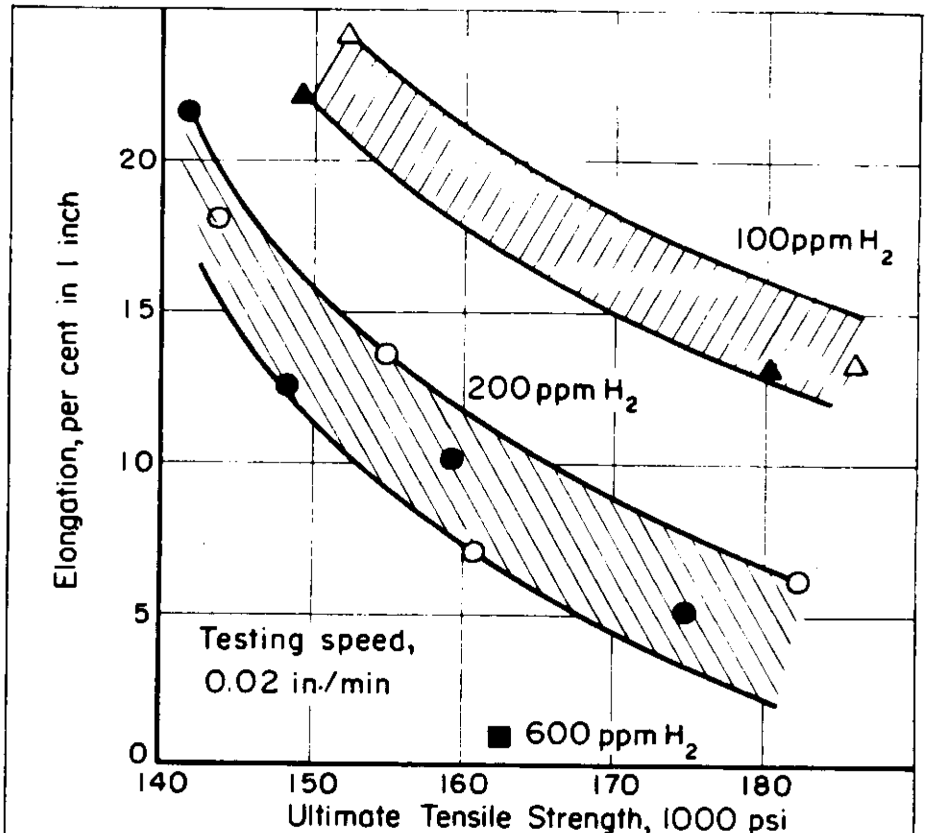
Notched Stress-Rupture Characteristics of Ti-8% Mn Sheet, Heat No. A3810-B11

NOTCHED STRESS RUPTURE (SUSTAINED LOADING) CHARACTERISTICS OF COMMERCIAL 8% MN SHEET

HEAT NO.	H_2 (PPM)	STRESS (% OF NOTCH U.T.S.)	TIME TO FRACTURE (HOURS)
AC	420	80%	1.5, 1.5
AB	275	80%	23.8, 33.8
DG	260	74%	12
CD	254	80%	0.3, 1.0
DL	169	80%	137

Figure 15

Notched Stress-Rupture Characteristics of Commercial Ti-8% Mn Sheet



EFFECT OF HYDROGEN CONTENT ON THE DUCTILITY OF HEAT-TREATED Ti-3 Mn COMPLEX ALLOY SHEET

Figure 16

Discussion by M. Parris (Battelle Memorial Institute)

SHEAR CRACKING OF COMMERCIAL Ti-8% Mn SHEET

by

Lt G. T. Hahn

One of the difficulties presently being encountered in the fabrication of titanium sheet is the problem of shear cracking. Fabricators and users of titanium sheet are confronted with instances of severe cracking in the plane of sheared edges. The following is a brief review of experience shared by airframe manufacturers:

1. Shear cracking is restricted to, or at least predominant in alloy material, such as commercial Ti-8% Mn sheet. Susceptibility to cracking varies from heat to heat, is very prominent in some heats, and not evident in others.

2. The shear cracks, diagonal or horizontal in nature, appear on edges on both sides of the shear cut. The cracks seriously affect tensile properties and fatigue life.

3. There appears to be no correlation between normal tensile properties and tendency to shear crack.

4. No remedy, other than the removal of defective edges by some method other than shearing, is known.

A routine study of the shear cracking phenomenon was undertaken at the Materials Laboratory, Directorate of Research, Wright Air Development Center. The material used, 12 different heats of commercial Ti-8% Mn sheet that had exhibited shear cracks during fabrication, was made available by Consolidated Vultee Aircraft Corporation. Shearing operations were performed on a Columbia Machinery and Engineering Corporation squaring shear, 3/8" capacity (mild steel), 48" long, 24" in gap, type 0604L. Observations made pertaining to the geometry of the cracks, microstructure, and possible connection with hydrogen contamination are discussed in this paper.

Geometry of Cracks. Photographs of typical examples of shear cracking are shown in Figure 1 and 2. At this magnification (10 to 15 x) the cracks appear to be continuous, either diagonal, horizontal, or diagonal with horizontal components.

A definite relationship was observed between the orientation of the diagonal cracks and the shear operation. As shown schematically in Figure 3, cracks in the supported edge were oriented diagonal to the edge of the shear blade. Cracks located in the opposite edge (the cut-off piece), on the other hand, traced more or less parallelto the edge of the shear blade. To check this observation a circular blank was punched from one of the sheets. The punch, shown in Figure 4, was not flat, but was designed with a hollow or saddle. The action of the punch therefore corresponded to that of two opposed shear blades. Cracks were encountered in the supported piece and in the edges of the circular blank (see Figure 4). Cracks located in the supported edge were directed diagonal to the shearing edge of the punch, while cracks in the edge of the blank were oriented parallel to the shearing edges.

These observations indicate that cracks on opposite sides of the sheared interface are oriented diagonally with respect to each other. Still, in most instances cracks on one edge were accompanied by cracks on the mated opposite edge. This suggests that while the cracks are not continuous across the interface they may have initiated at some common fault or defect.

<u>Microstructure of Shear Cracks.</u> Examples of shear cracks photographed under higher magnification are presented in Figures 5 through 10. Shear cracks in Figures 5 through 9 appeared to be continuous diagonal type cracks macroscopically. The photograph shown in Figure 10 shows a portion of a horizontal type crack.

The photographs indicate that all shear cracks are generally discontinuous in nature. Cracks which appear to be diagonal at low magnification are composed of a series of horizontal cracks, discontinuous (Figure 6), or connected in the form of a step ladder. This arrangement suggests that shear cracking is related to planes of weakness existing in sheet parallel to the plane of rolling, such as the separation of a deck of playing cards under shear or tensile forces. Planes of weakness extending across the shear interface would account for a common defect and mated cracks on opposite edges.

<u>Microstructure of Ti-8% Mn Sheet.</u> The microstructure of the sheets studied exhibited a pronounced banding. This banding, evident in Figures 5 through 10, and also in Figure 11, appears as light, single phase stringers in a more heavily etched, equiaxed matrix. The same field shown in Figure 11 under bright lighting is presented in Figure 12 under polarized light. The light bands or stringers appear dark, and were not optically active under polarized light. Since the alpha modification of titanium is optically active and the beta modification is not active, it is concluded that the stringers are manganese-rich regions of retained beta.

Shear cracks followed the contours of the bands or stringers. In some instances (see Figures 8, 9, and 10) the shear cracks were located at the boundaries of the stringers. This suggests that the boundaries of the beta stringers in the plane of rolling may be one of the sources of weakness responsible for shear cracking.

Hydrogen Contamination. The possibility that shear cracking is a manifestation of hydrogen contamination was investigated. Hydrogen analyses were obtained for the different heats of Ti-8% Mn sheet subject to shear cracking, and the results are shown in Figure 13. The heats are listed in the table in order of susceptibility to shear cracking. Heats which exhibited a continuous series of cracks on any one edge were classified as severe; with occasional cracks, as moderate; and with one or two isolated cracks, as mild.

The analyses indicate that high hydrogen and low hydrogen contents were associated with each category, and that there was no correlation between hydrogen content and susceptibility to shear cracking. In addition samples of heats exhibiting severe cracking were subjected to a vacuum annealing treatment to remove hydrogen, and duplicate samples were given the same thermal treatment (24 hrs at 1200°F followed by a furnace cool) in helium atmosphere. These treatments reduced slightly the severity of the cracking. However, no difference in extent was observed for the dehydrogenated vacuum annealed samples and the helium annealed samples. These results suggest that shear cracking is not related to hydrogen contamination or hydrogen embrittlement.

Summary and Conclusions

1. Cracks were observed in sheared edges of commercial Ti-8% Mn sheet. Macroscopically the cracks appear to be continuous, either diagonal, horizontal, or diagonal with horizontal components. The orientation of diagonal cracks is related to the shearing operation.

2. Under higher magnification, shear cracks appear to be relatively discontinuous. Diagonal cracks are composed of small horizontal units, discontinuous, or connected in the form of a step ladder. The horizontal nature of shear cracks suggests that this phenomenon is related to planes of weakness existing in sheet parallel to the plane of rolling.

3. Microstructures of the Ti-8% Mn sheet exhibited a pronounced banding effect thought to be stringers of manganese-rich, retained beta. Shear cracks followed the contours of the banding and in some instances were located at stringer boundaries. It is suggested that beta-stringers may be one of the sources of weakness responsible for shear cracking.

4. Shear cracking does not appear to be related to hydrogen contamination or hydrogen embrittlement.

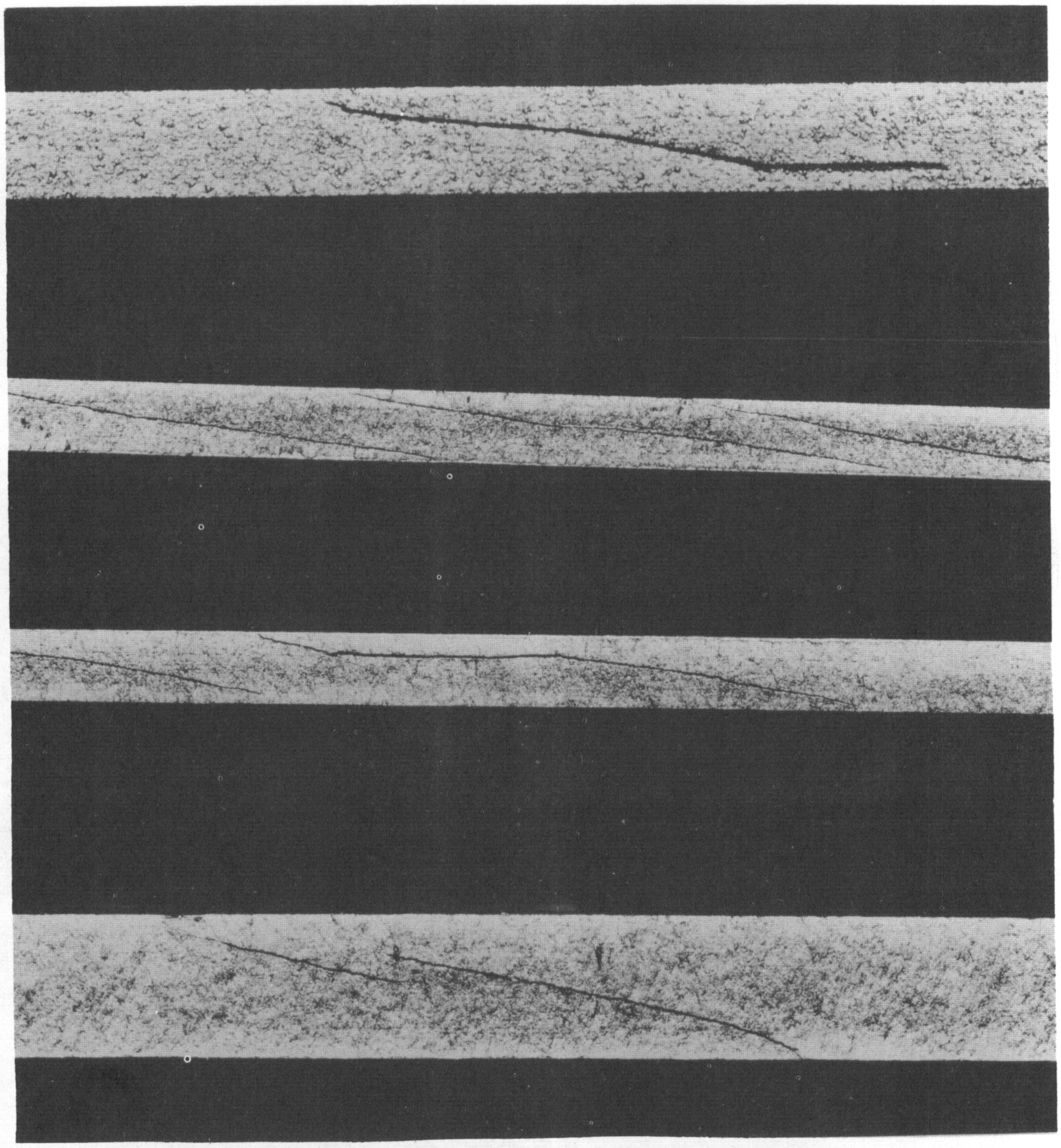


Figure 1

Shear cracked edges, commercial Ti-3% Mn Sheet, as sheared and etched. Magnification: 10x - 15x. Etchant: 47cc conc. HNO_3, 3 cc conc. HF, 50 cc H_2O

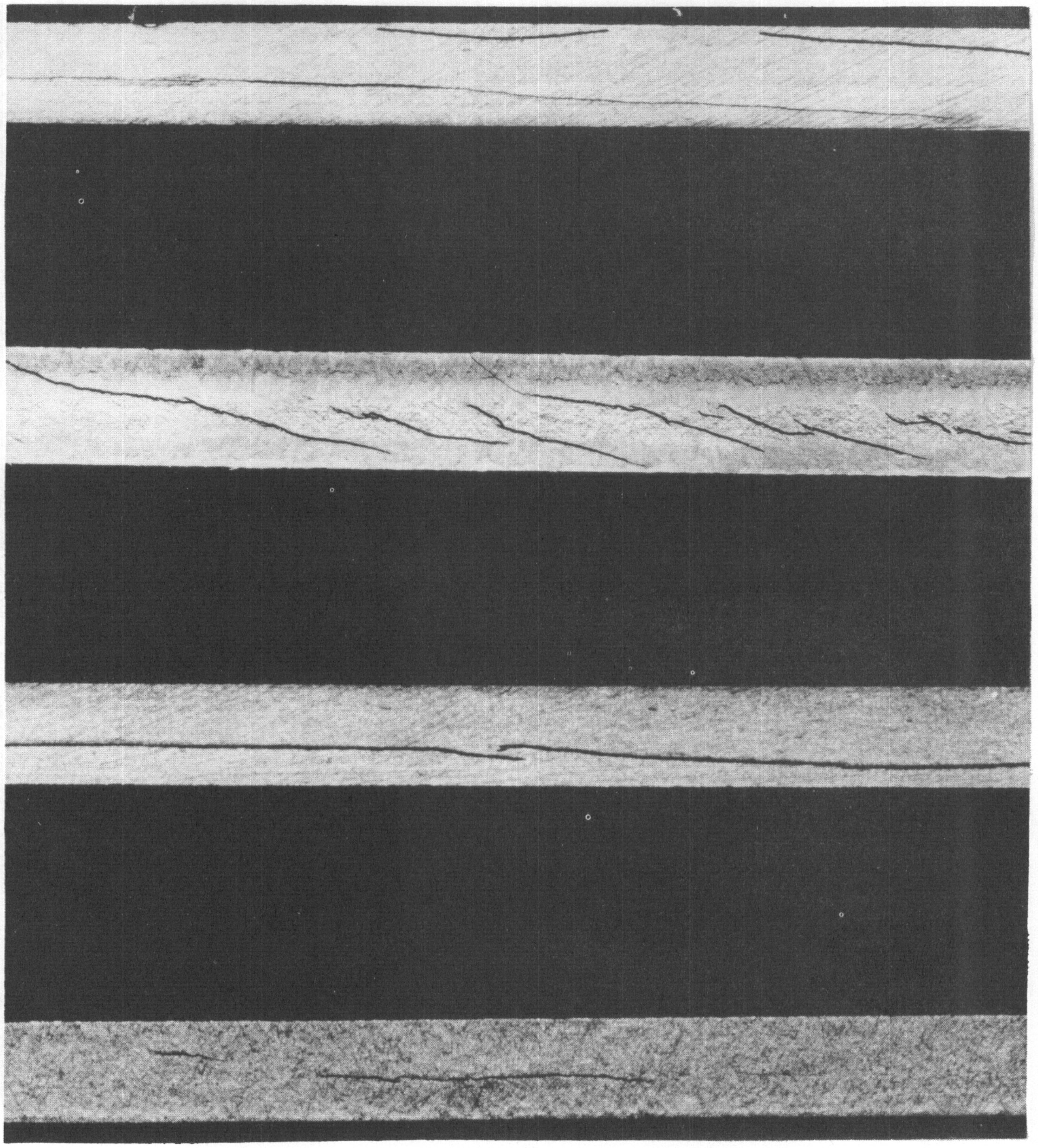


Figure 2

Shear cracked edges, commercial Ti-8% Mn sheet, as sheared and etched. Magnification: 10x-15x. Etchant: 47cc conc. HNO_3, 3cc conc. HF, 50cc H_2O.

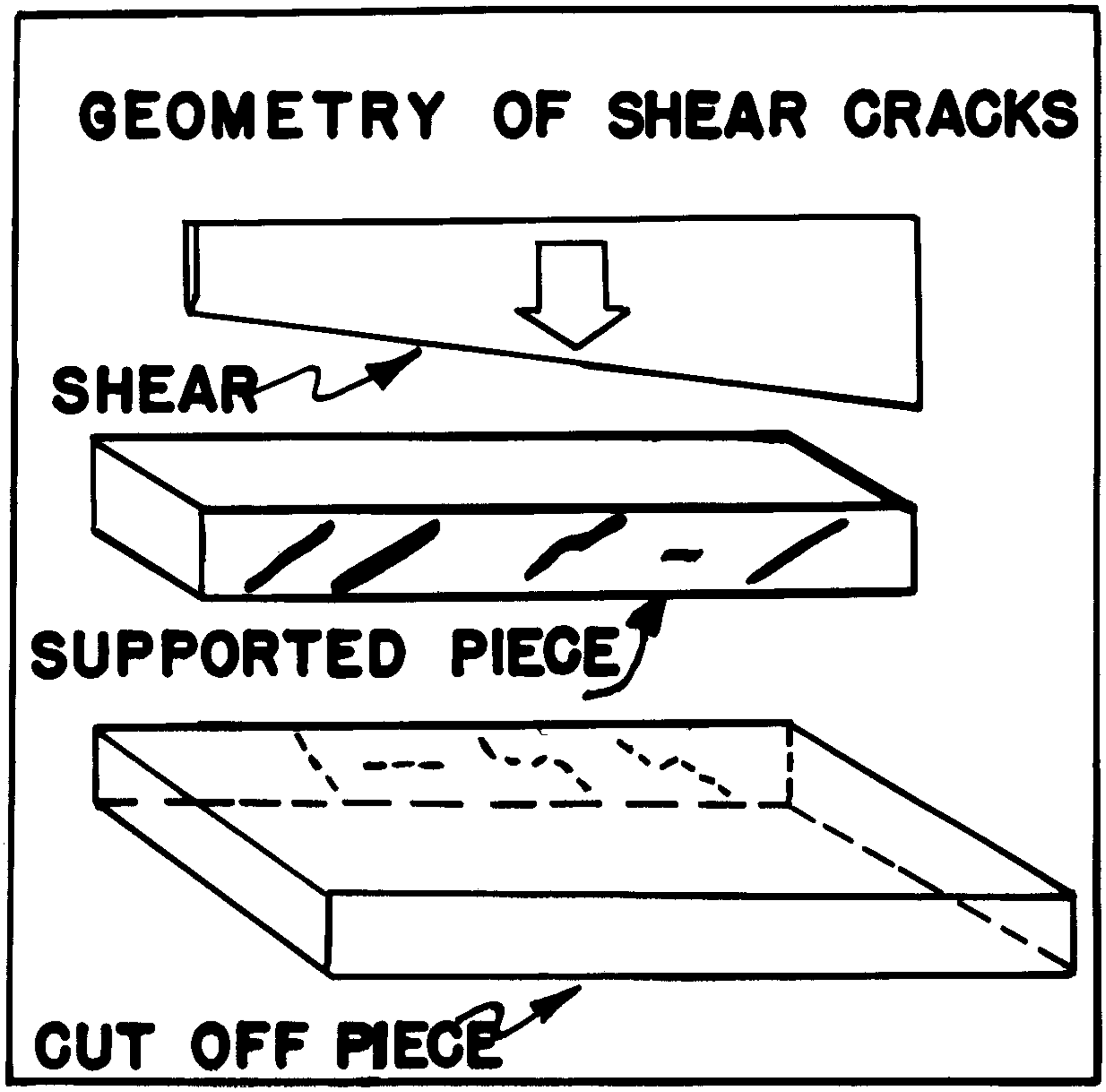


Figure 3

Geometry of shear cracks (Shearing operation)

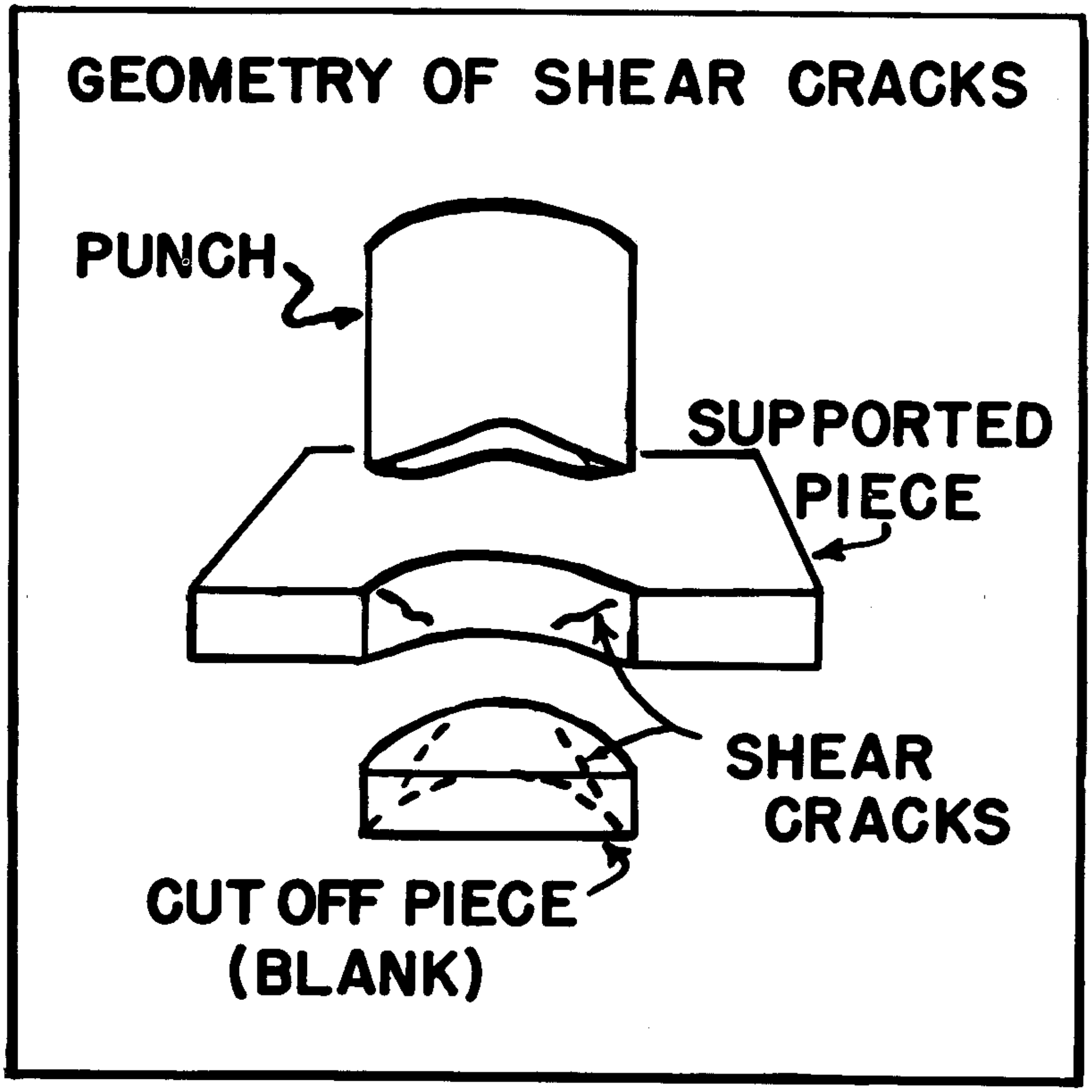


Figure 4

Geometry of shear cracks (Punching operation)

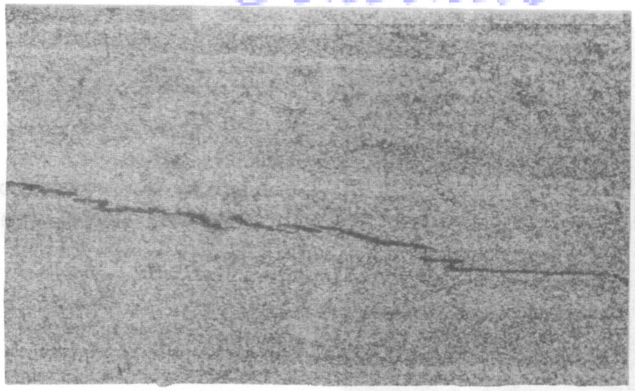


Figure 5. Portion of a diagonal type shear crack.

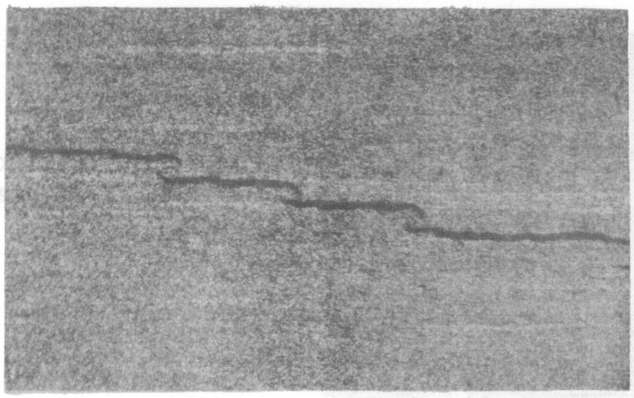


Figure 6. Portion of a diagonal type shear crack.

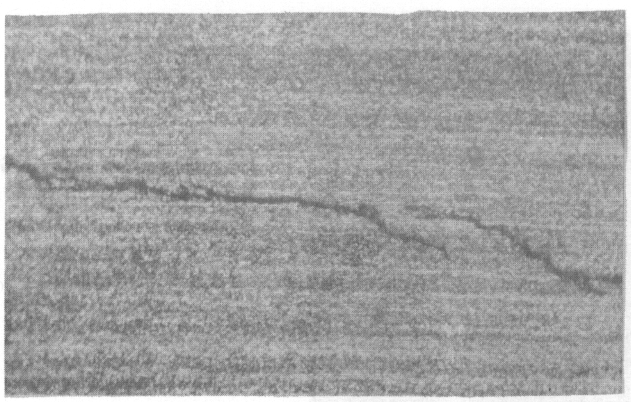


Figure 7. Portion of a diagonal type shear crack.

Examples of shear cracks in Ti-8% Mn sheet, polished and etched. Magnification: 100x. Etchant: 10 cc conc. HNO_3, 2 cc conc. HF, 88 cc H_2O.

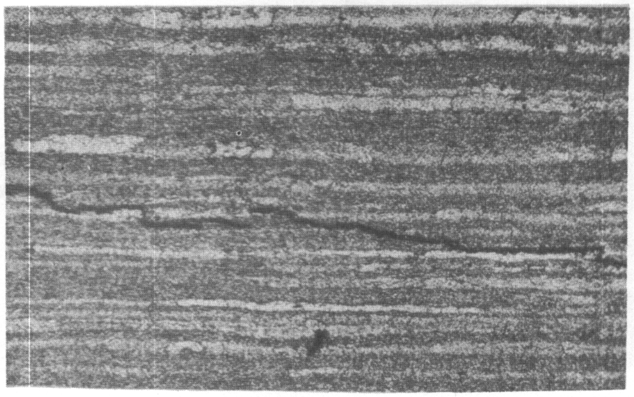


Figure 8. Portion of a diagonal type shear crack.

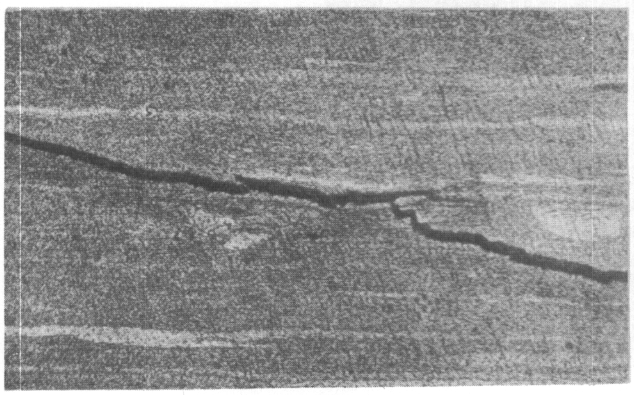


Figure 9. Portion of a diagonal type shear crack.

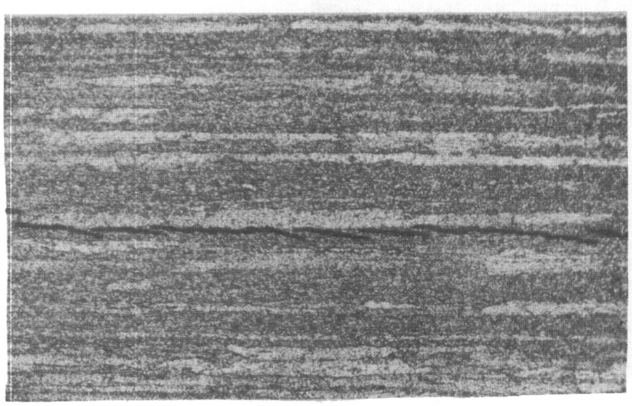


Figure 10. Portion of a horizontal type shear crack.

Examples of shear cracks in Ti-8% Mn sheet, polished and etched. Magnification: 100x. Etchant: 10cc conc. HNO_3, 2cc conc. HF, 88cc H_2O.

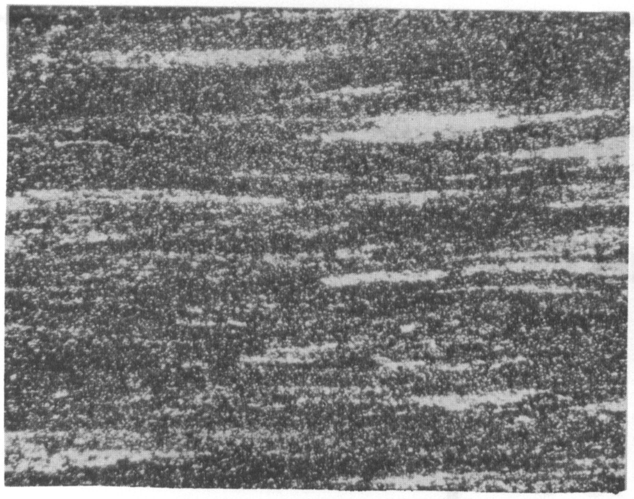


Figure 11. Commercial Ti-8% Mn sheet, longitudinal edge that exhibited shear cracks. Structure throught to be beta stringers (light) in equiaxed alpha-beta matrix (dark).

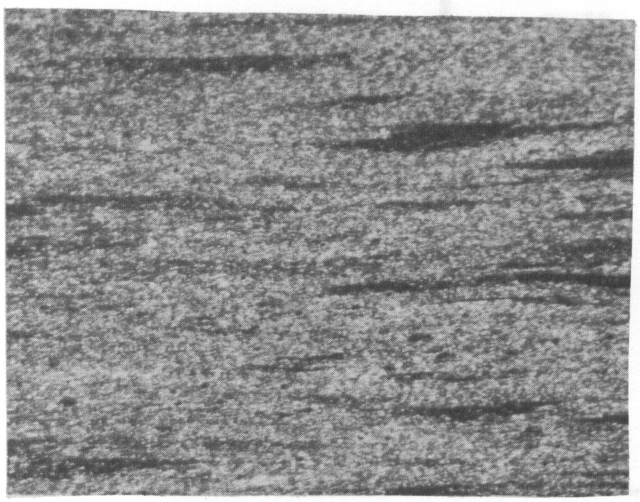


Figure 12. Same area as Figure 11 under polarized light. Structure thought to be beta stringers (dark and not optically active) in equiaxed alpha-beta matrix. (light and optically active).

Magnification: 100x. Etchant: 10cc conc. HNO_3, 2 cc conc. HF, 88cc H_2O.

HYDROGEN CONTENT OF 8% Mn SHEET EXHIBITING SHEAR CRACKS

HEAT NO.	H_2 (PPM)	EXTENT
R2A-277	194	SEVERE
R2A-555	185	
A3962-11	154	
R2A-236-2B	126	
R2A 266-4A	205	MODERATE
A-5534-BMG	155	
A 3609- 18	135	
A-5220-4	115	
R2A 318-Z3A	254	MILD
A 3591 -4	145	
R 2A -277	142	

Figure 13

Hydrogen Contents of Ti-8% Mn sheet exhibiting shear cracks.

THE EFFECTS OF HEAT TREATMENT ON HYDROGEN EMBRITTLEMENT OF A HIGH STRENGTH TITANIUM ALLOY

by

Lt E. F. Erbin

To date most of the information available on the embrittlement of titanium alloys by hydrogen has been confined to material which is in the annealed condition and possesses relatively low strength. In most if not all of the present day applications of titanium alloys these low strength properties are acceptable. Undoubtedly as higher strengths and greater elevated temperature stability are demanded the heat treatment of titanium alloys will become more popular and see wide applications. In light of this situation, interest is focused on the behavior of high strength heat treated titanium alloys when contaminated with hydrogen. Whether a titanium alloy becomes more or less susceptible to hydrogen embrittlement when tensile strengths on the order of 170,000 psi are approached would both govern its use as a heat treatable material and regulate the acceptable amount of hydrogen in the as-received condition.

Information on this aspect of hydrogen embrittlement has been obtained in investigations at the Materials Laboratory, Directorate of Research, WADC and at Battelle Memorial Institute. The material employed in this work was the semi-commercial 3 Manganese Complex titanium alloy which is capable of being heat treated to high strength. The nominal composition of this alloy is 3 Mn-1 Fe-1 Cr- 1Mo - 1V - balance titanium.

In recent work performed at WADC, a heat of 3 Mn Complex alloy was first vacuum annealed to a low hydrogen level. Subsequently the material was finished rolled to 1/2 inch round stock at a temperature in the alpha-beta region, hydrogenated to 120, 220 and 300 ppm. and then heat treated to a high strength level of 170,000 psi ultimate tensile strength. The heat treatment consisted of solution treating at 1300°F for 1 hour followed by water quenching and aging at 900°F for 8 hours. This heat treatment is designed to give a strength level of 170,000 psi UTS combined with good ductility in the absence of hydrogen of 50% reduction in area and 18% elongation in 1 inch. However the ductility of the material will be shown to be markedly effected by the hydrogen content. The heat treated 3 Mn-Complex specimens were tested in tension at various testing speeds and temperatures. The speed of the tensile tests was controlled by a strain pacer. The temperature of the specimens was kept constant during testing by means of a liquid bath surrounding the specimens. Figure 1 shows, for measurements at room temperature, the strain rate dependence of the degree of embrittlement. In this figure ductility expressed as reduction in area of the specimen is plotted as a function of the testing speed. The testing speeds represented here vary by a factor of 100. The ductility of the material containing as little as 120 ppm hydrogen is seen to be seriously impaired at the slow testing speed. Faster tests result in increased ductility. The effect of testing temperature on the ductility of the 3 Mn Complex containing increasing amounts of hydrogen is shown in Figure 2 for a testing speed of .005"/minute. At this testing speed and in faster tests it was observed that a minimum in the tensile ductility occurs in the vicinity of room temperature. On the basis of these data, slow speed tensile testing (0.005"/minute) at room temperature was chosen to determine the relative degree of embrittlement in this alloy when in various heat treated states. Using these testing conditions, the effect of hydrogen on the ductility of the 3 Mn-Complex titanium alloy heat treated to 170,000 psi UTS is shown in Figure 3. At a very low hydrogen level of 30 ppm this high strength material exhibits excellent ductility, the reduction in area of the specimen being 45%. Increasing amounts of hydrogen progressively lower the ductility and above 200 ppm the reduction in area is reduced to below 10%. At this high strength level then, this particular alloy is shown to be severely embrittled by hydrogen at very low hydrogen contents.

To illustrate the effect that the heat treated strength has upon the alloy's reaction to increasing hydrogen content, curves for the 3 Mn Complex in the low strength annealed condition and in the high strength heat treated state are plotted together in Figure 4. The ductility of the two strength levels are seen to be approximately the same in the absence of hydrogen. A small amount of hydrogen (100 ppm) decreases the reduction in area of the heat treated material to one half its original value; for the annealed material, more than 300 ppm are required to give the same effect. At 200 ppm the high strength material has less than 10% reduction of area in this test. The reduction in area of the annealed material is still greater than 10% at 700 ppm hydrogen. There is little doubt that this difference in hydrogen tolerance is real and is due in most part to the difference in heat treatment and strength properties.

The work of Frost et. al. [1] at Battelle Memorial Institute, under Air Force Contract, further illustrates the role of heat treated strength in determining hydrogen tolerance. This group, working with another heat of the 3 Mn Complex of similar interstitial and alloy analysis, first hydrogenated the material to various levels and then heat treated it to several strengths. Three of these strengths, 120,000, 170,000 and 180,000 psi UTS were obtained by the quench and age type of treatment already described. Each heat treatment employed and the resultant mechanical properties are described in Table 1. Test conditions were the same as those used on the 170,000 psi material previously described. The room temperature ductility characteristics of each heat treated condition are plotted as a function of hydrogen content in Figure 5. The 120,000 and 170,000 psi tensile strength materials have about the same reduction in area in the absence of hydrogen. However, the deleterious effect of increasing hydrogen content is very prominent at the high strength level while at 120,000 psi as much as 300 ppm hydrogen is seen to have little effect. When heat treated to 180,000 psi UTS this alloy has good tensile ductility although less than that at lower strength levels. However at this strength level the alloy becomes seriously embrittled at a hydrogen level generally considered quite acceptable i.e. 100 ppm. Beyond 200 ppm this high strength material has no measurable reduction in area. It would appear that as strength properties increase, lower hydrogen contents become critical.

In Figure 5 the curve labeled 150,000 represents the 3 Mn Complex alloy quenched from the alpha-beta range but not aged. In the quenched condition the alloy has a tensile strength of 150,000 psi and 55% reduction in area. The microstructural configuration is this condition differs from the quenched and aged material but the curve representing its ductility as a function of hydrogen content falls about where one might expect, if a strength level dependency exists.

However, the significance of a dependency on strength level alone is difficult to rationalize. Microstructure and thermal treatment would be expected to play an important role in controlling the reaction of an alloy to hydrogen. It might be pointed out that alpha alloys react differently to hydrogen than do alpha-beta alloys and that the solubility of this interstitial element is far greater in the high temperature beta phase than in the alpha phase.[2] Consequently the alpha to beta ratio should have an important influence. The configuration of the alpha phase would also be expected to be significant. Furthermore, prior thermal history may control the microdistribution of the hydrogen.

In as much as all the material represented in Figure 5 has been quenched from the alpha-beta range during heat treatment it is interesting to note the effect that aging temperature has upon the hydrogen tolerance. The 150,000 psi strength level represents the material as quenched. The low aging temperature of 800°F and 900°F used for the two highest strength levels is seen to be very deleterious while the higher temperature of 1100°F has a beneficial effect on the hydrogen tolerance. Of course the amount and configuration of alpha is different as a result of aging at each of these temperatures.

The importance of microstructure and thermal treatment is emphasized by the data presented in Figure 6. The curves represent the Complex alloy in two heat treated conditions. One was continuously cooled from the annealing temperature of 1300°F, while the other was quenched from solution temperature and aged. Both of these conditions exhibit the same strength and ductility at low hydrogen levels. However a noticeable difference in their reaction to increasing hydrogen content is apparent. The addition of 300 ppm hydrogen does not effect the tensile ductility of the quenched and aged material. The same hydrogen level in the annealed alloy reduces the tensile ductility to 1/2 of its original value. A major difference in the two heat treatments is of course the time at temperature.

It has been shown that the reaction of an alloy to hydrogen when in the annealed condition is not necessarily representative of its behavior when heat treated. The time and temperatures employed during heat treatment appear to have a significant effect on the hydrogen tolerance of alpha-beta alloys. Increased sensitivity of titanium alloys to hydrogen embrittlement can be expected as higher strengths are approached through the use of heat treatment. Hydrogen contents that do not cause embrittlement when the material is in the annealed condition, may become critical at higher strength levels. These comments and data merit a new note of dampened enthusiasm for the use of hydrogen contaminated titanium alloys and should serve as a warning to those who plan the use of these alloys in the high strength, heat treated condition.

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1. Private communication from P. Frost and M. Parris, Battelle Memorial Institute.

2. Lenning, Craighead and Jaffee "Constitution and Mechanical Properties of Titanium-Hydrogen Alloys", Journal of Metals (March 1954).

D I S C U S S I O N

McClintick: I notice that you use in/min. cross head speed. Strain rate is generally reported as in/in/min.

Is there a conversion factor between inches per minute cross head speed and inches per inch per minute strain rate?

Erbin: There is a qualitative conversion between cross head speed and true strain rate. Below the yield point in a tension test the strain rate is approximately 1/3 of the cross head speed. Beyond the yield point the strain rate approaches the testing speed and beyond the ultimate load the two are nearly the same.

Shinn: There is no conversion factor between head travel in inches per minute and strain rate in inches per inch per minute that will hold for all tensile testing. The conversion factor between testing speed and strain rate will vary with the material tested, the specimens geometry and the tensile testing machine employed.

In these tests the strain rate in itself was not considered significant but rather the qualitative rates of testing and the time required to fracture the specimen were the significant feature.

Hill: I would like to have the reference to the information that the various heat treatments and aging you have done here can be carried out without loss or change of hydrogen concentration. Is that information published? I see that a heat treatment in vacuum will degas the specimen but a heat treatment in air will not. In the case of iron this is certainly not true. Is there a reference in the literature where this fact has been published or has it been shown here? How do you know that you are not changing the hydrogen concentration during these aging treatments?

Erbin: Analyses were made before and after the thermal treatments and showed no change in hydrogen concentration. The material was first vacuum annealed, then rehydrogenated to various levels and then heat treated. It was analyzed after the vacuum anneal, after the hydrogenation treatment and after the heat treatment cycle. There was no noticeable change in hydrogen level during heat treatment in air.

Coontz: Have you shown that there is no change in the other interstitial elements during vacuum annealing?

Erbin: No, I can't say that we have shown this. However, it is generally felt that there is little loss in these interstitial elements, that is oxygen, nitrogen and carbon, during vacuum treatment. We are checking this point at the present time.

Mallett: In one of your slides, you showed a plot of ductility versus temperature and showed three points and conclude that you get a minimum in the ductility at room temperature. I do not believe that with three points you can conclude this. The minimum may fall anywhere between the two extremes.

Erbin: You will recall that I said " a minimum occurs in the vicinity of room temperature". In the figure that you cited, the material of highest hydrogen content was completely embrittled at room temperature. We have other data taken at higher testing speeds in which the embrittlement is less severe and which show this ductility trough in the vicinity of room temperature. Again only three temperatures were investigated but in all material containing more than 200 ppm hydrogen, a minimum in the ductility was noticed between +200°F and -120°F. On the basis of this we concluded that testing at room temperature, at a slow rate would be a severe test.

Mallett: It lends a significance to a room temperature test which I do not believe is reported in the literature. If you extrapolated the lines in your figure you will see that the minimum could lie on either side of room temperature.

Erbin: That is true. However at the high hydrogen levels, the curve of reduction in area versus temperature cannot decrease further. Therefore the minimum in this curve occurs either at or above room temperature. In this case the ductility has reached a minimum value at room temperature.

For the purpose of illustrating relative differences we thought testing at room temperature would be a severe and useful test.

Hill: I believe it should be pointed out that the effect of heat treatment on the hydrogen embrittlement of titanium is identical to that occuring in steel. Much might be gained by drawing from the information available on the hydrogen embrittlement of steel.

Erbin: And conversely, from what we learn about the hydrogen embrittlement of titanium, where we are working with larger concentrations of hydrogen, we may throw some light on the hydrogen problem in steel.

TABLE 1

Effect of Thermal Treatments on Mechanical Properties
of the Three Mn-Complex Alloy

	Thermal Treatment		Ultimate Tensile Strength	Reduction* In Area %
1.	1300°F-1Hr-W.Q.	900°F-8Hr	170,000	52
2.	1300°F-1Hr-W.Q.	800°F-48Hr	180,000	30%
3.	1300°F-1Hr-W.Q.	1100°F-8Hr	120,000	55%
4.	1300°F-1Hr-W.Q.		150,000	50

* Low hydrogen content (less than 50 ppm)

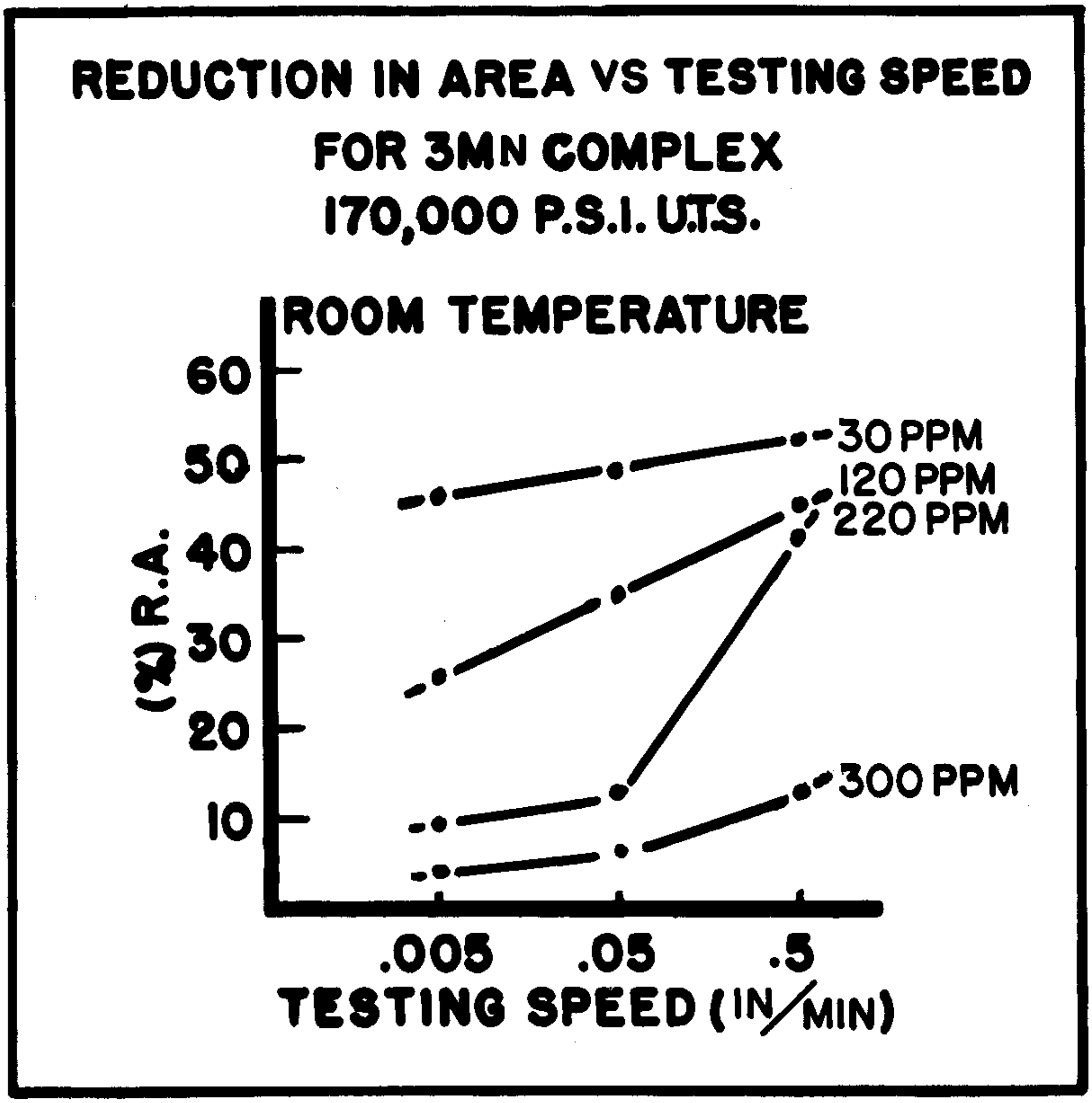

Figure 1

Effect of Testing Speed on the Tensile Ductility of the 3 Mn-Complex Titanium Alloy

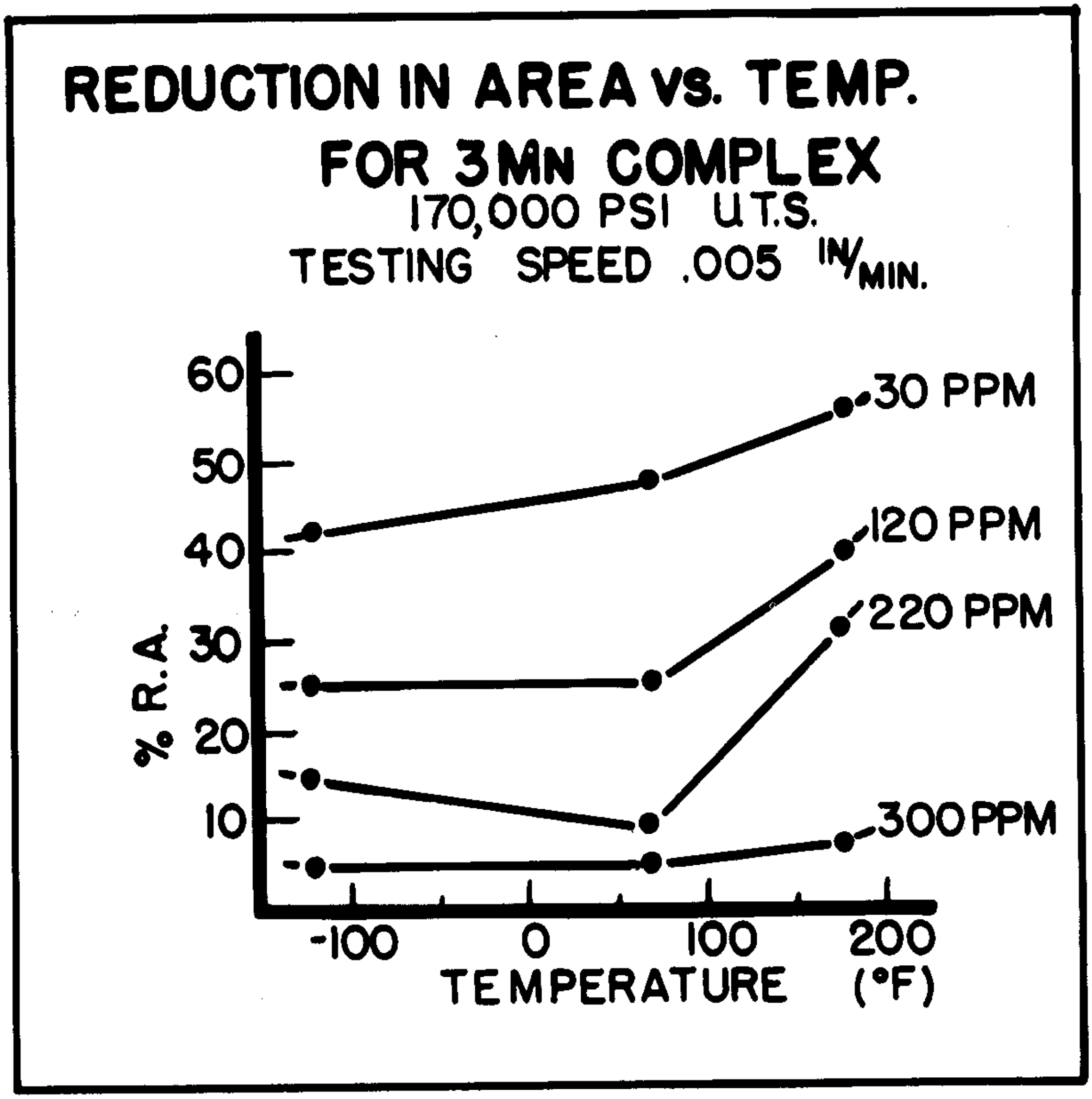

Figure 2

Effect of Testing Temperature on The Tensile Ductility of the 3Mn-Complex Titanium Alloy

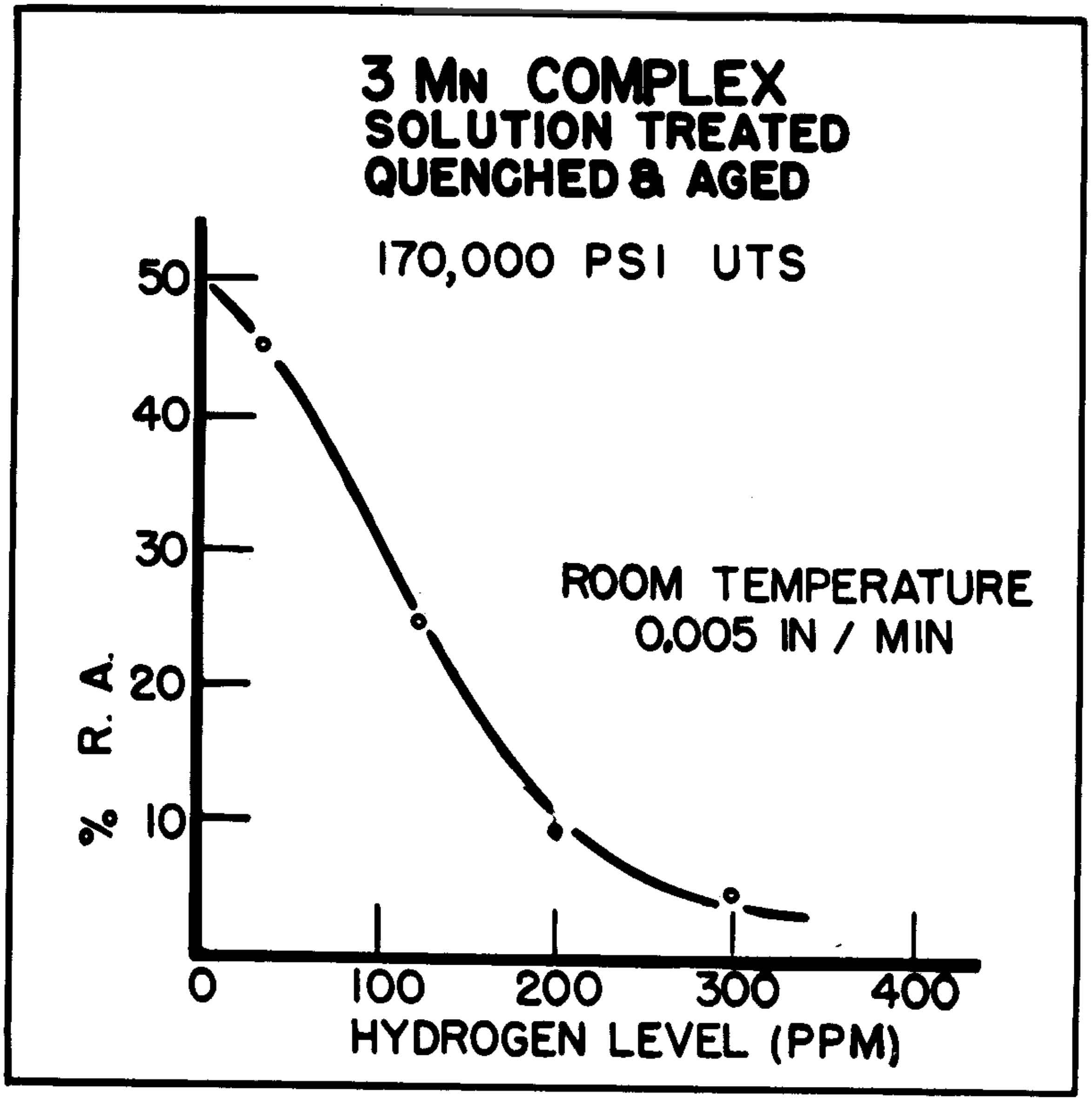

Figure 3

Effect of Hydrogen Content on Tensile Ductility of the 3 Mn-Complex Titanium Alloy

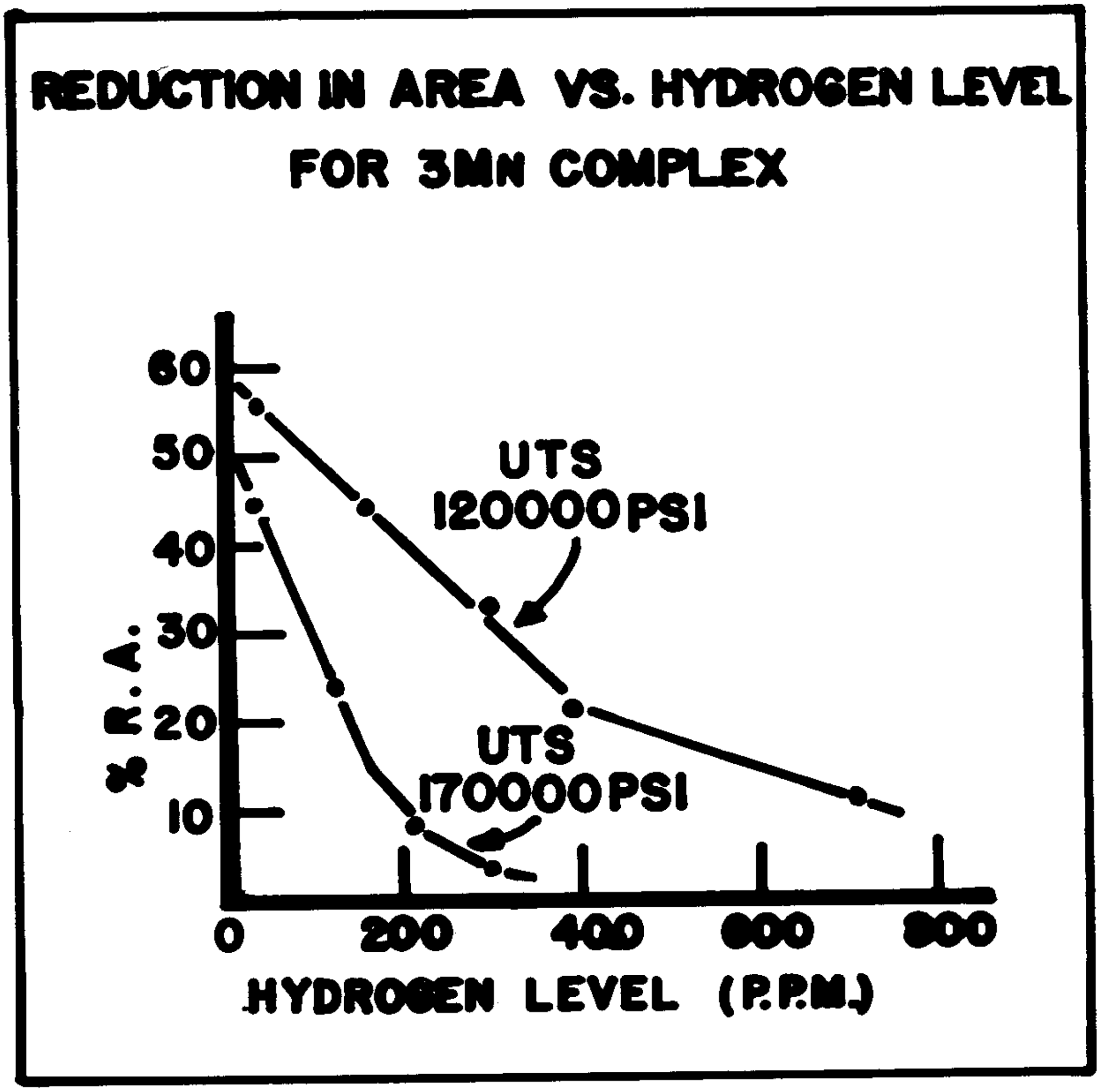

Figure 4

Effect of Heat Treatment on the Hydrogen Embrittlement of the 3Mn-Complex Titanium Alloy

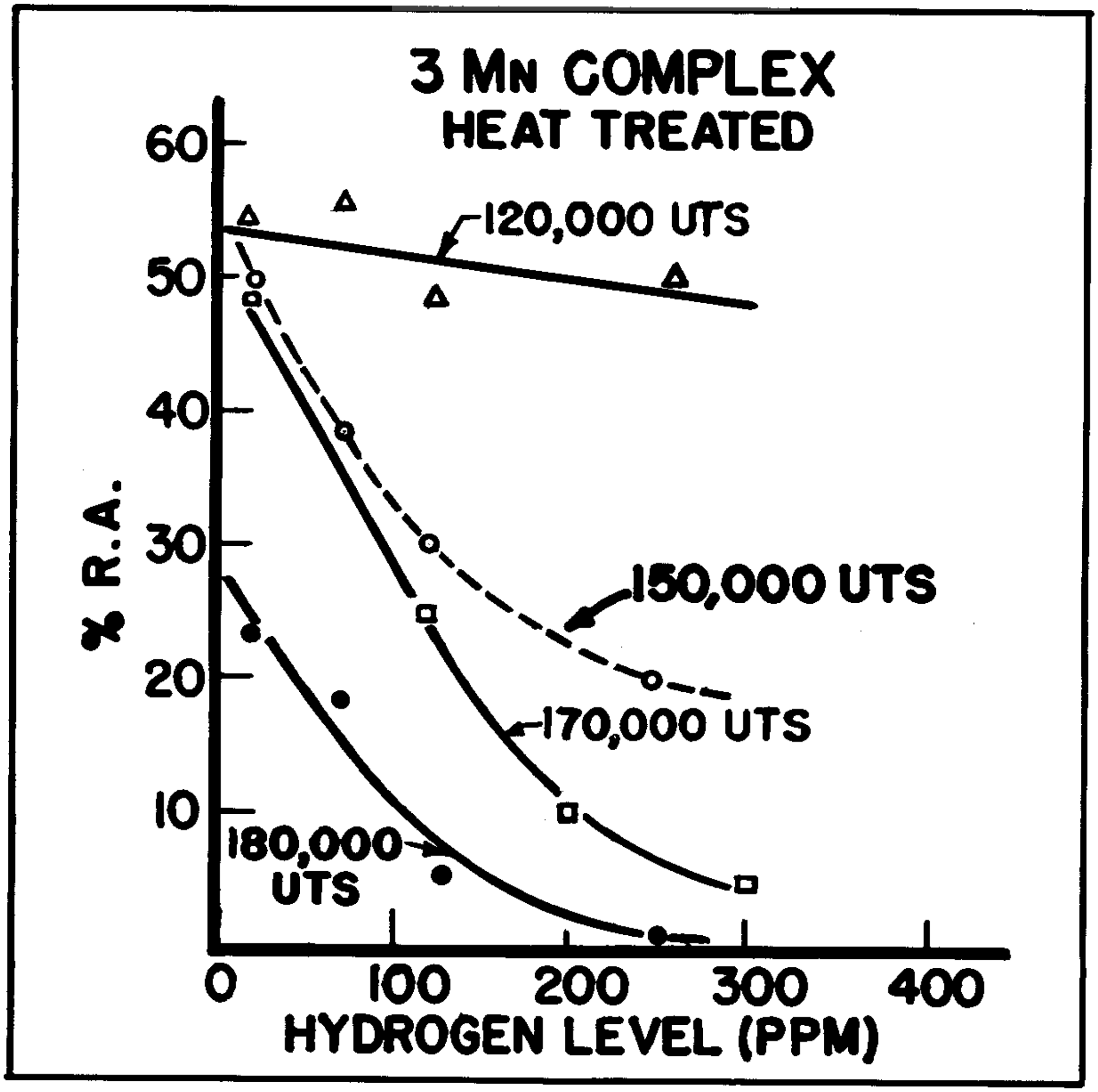

Figure 5

Effect of Heat Treated Strength on the Hydrogen Embrittlement of the 3 Mn-Complex Titanium Alloy

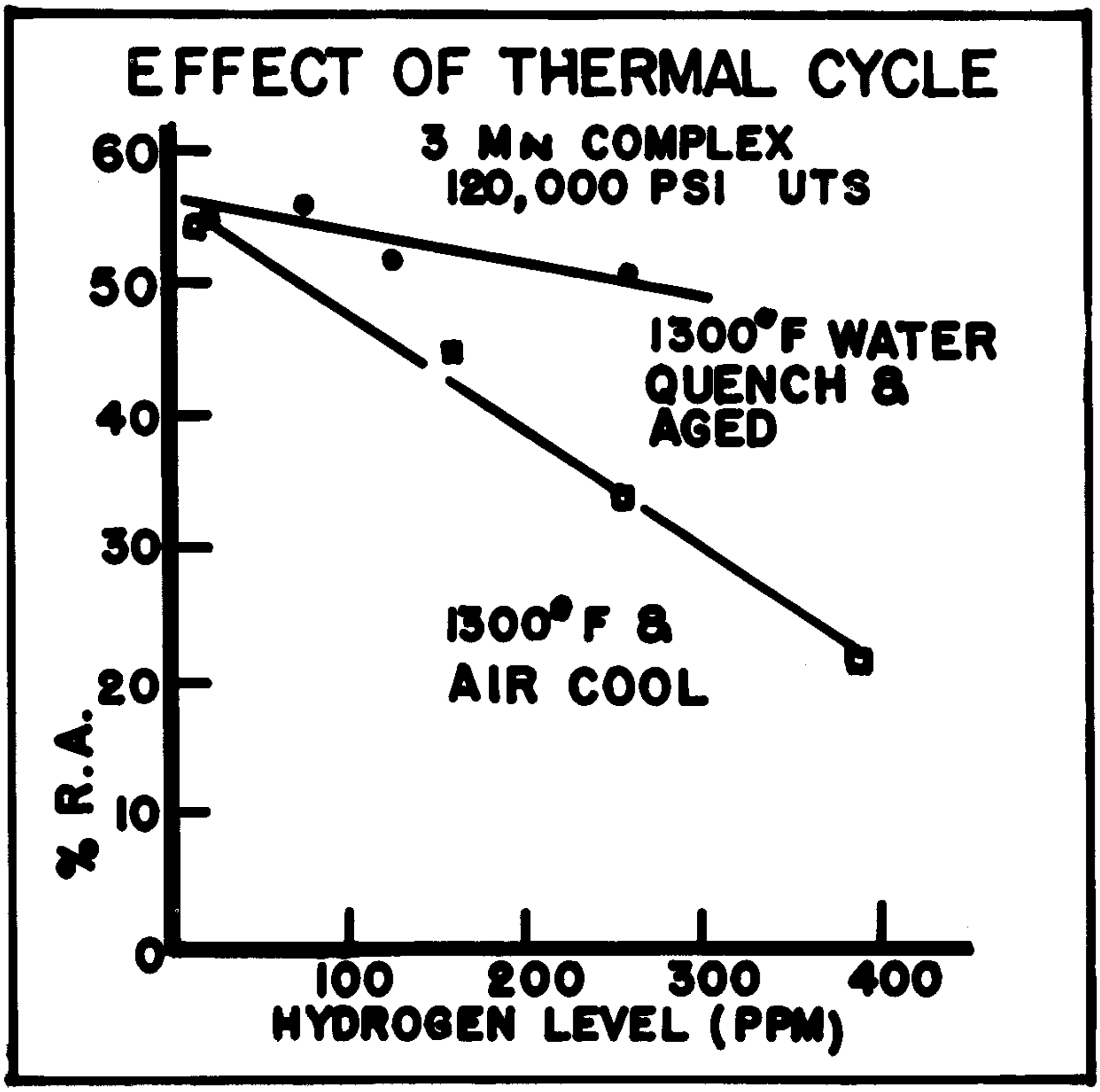

Figure 6

Effect of Type of Heat Treatment on the Hydrogen Embrittlement of the 3 Mn-Complex Titanium Alloy

CREEP EMBRITTLEMENT OF TITANIUM ALLOYS

by

Lt D. A. Wruck

I. INTRODUCTION

When alpha-beta titanium alloys are exposed to conditions involving stress, time and temperature they often show a tendency to lose some of their ductility as measured in subsequent room temperature tensile tests, and in severe cases become very brittle. One cause of this "creep embrittlement" is improper thermal treatment that leaves the structure in an unstable form. This emanates from the fact that titanium exists in two allotropic forms; namely, hexagonal close-packed alpha and body-centered cubic beta. In pure titanium the alpha phase is stable up to 1625°F at which point it transforms into beta titanium. The beta phase is stable from 1625°F to the melting point of approximately 3150°F. The addition of certain alloying elements tends to stabilize the beta phase to lower temperatures. The principal metallic beta stabilizing elements are iron, chromium, molybdenum, manganese and vanadium. The interstitial impurity, hydrogen, is also a beta stabilizer.

In addition to lowering the temperature at which beta transforms to alpha upon cooling, these stabilizing elements also tend to impart a degree of sluggishness to the transformation. Therefore, with sufficiently high alloy contents and cooling rates much of the beta phase may be retained in a metastable condition at room temperature. This metastable beta can subsequently transform under certain conditions of stress and temperature. At relatively low temperatures (100° - 800°F), the mechanism of this transformation may be such that the alloy becomes brittle. This loss of ductility caused by transformation of the metastable beta is termed "transformation embrittlement" in this paper. The mechanism of transformation embrittlement is not clearly understood. It appears to be associated with an aging phenomenon wherein embrittlement is caused by precipitation or coherency of a finely dispersed phase. P. D. Frost, et al[1], of Battelle Memorial Institute, have formulated the supposition that a transition phase is encountered in the transformation from beta to alpha. This tentative phase is supposedly of a pseudocubic structure presently called "omega", and, although it is associated with embrittlement, the manner in which it induces embrittlement is not known. Other theories on transformation embrittlement deal with coherency hardening and dispersion hardening.

In those instances where the fabricating procedures have produced an undesirable amount of metastable beta the alloy is frequently given a "stabilizing" treatment wherein the metal is annealed at a temperature above that at which transformation embrittlement is encountered. These temperatures are in the range of 1000° - 1300°F. The stabilizing treatment transforms the metastable beta to alpha and an enriched beta, and results in a structure that is stable under subsequent service conditions that involve stress and temperature.

A second possible source of creep embrittlement is that due to contamination by hydrogen. This may be completely independent of transformation embrittlement. It has been shown in previous sections of this report that hydrogen contamination has very deleterious effects on the "slow tensile" and rupture behavior of titanium alloys. It is also possible that hydrogen-contaminated specimens may become embrittled when exposed to conditions of stress, time and temperature even though they may be in a stable condition as far as transformation embrittlement is concerned. An investigation was therefore undertaken on Ti-140A (Ti-2Fe-2Cr-2Mo) to determine if stabilized structures would suffer creep embrittlement because of hydrogen contamination. This program included the following two phases:

1. A cursory investigation of transformation embrittlement to determine how several thermal treatments would affect the stability of hydrogen-free Ti-140A.

2. An investigation to determine the effect of hydrogen contamination on normally stable structures which are exposed to stress and temperature.

II. EXPERIMENTAL PROCEDURE AND RESULTS

This investigation was accomplished by subjecting specimens of various thermal histories and hydrogen levels to various conditions of stress, time and temperature. The specimens, thus treated, were evaluated by employing room temperature tensile tests[2].

A. Ti-140A bar stock was used to investigate the effect of various vacuum annealing treatments on beta stability. Specimens of this alloy were given the following thermal treatments:

1. Vacuum annealed at 1200°F for 24 hours; furnace cooled.
2. Vacuum annealed at 1200°F for 24 hours; air cooled.
3. Vacuum annealed at 1400°F for 24 hours; furnace cooled to 1200°F and air cooled.

The standard room temperature tensile test data as given in Figure 1 show that the alloy has good ductility and comparable tensile properties after each of the above thermal treatments. The 1400°F annealing treatment resulted in a somewhat softer structure than the 1200°F annealing treatments.

B. Unnotched tensile specimens of this vacuum annealed, low hydrogen material from the three thermal treatments were exposed to several conditions of stress, time and temperature. The first group was loaded at 80,000 psi and 200°F for 100 hours. Subsequent room temperature tensile tests indicate that very little transformation embrittlement took place in any of the specimens. These data are shown in Figure 2.

A second group of specimens given the three thermal treatments was loaded at 50,000 psi and 600°F for 500 hours. The higher temperature and longer time resulted in transformation embrittlement of the air cooled specimens, especially that which was annealed at 1400°F before air cooling from 1200°F. These data are plotted in Figure 3. It can be seen that the furnace cooled specimen suffered no appreciable embrittlement while exposed to the 600°F stressed conditions. The specimen that was air cooled after annealing at 1200°F shows a marked decrease in both percent reduction of area and percent elongation with a corresponding increase in strength. The greatest embrittlement took place in the specimen that was annealed at 1400°F before air cooling from 1200°F. Both the percent reduction of area and percent elongation were reduced to half their original values. These data indicate that the thermal treatment of 1200°F for 24 hours followed by furnace cooling will not result in transformation embrittlement under conditions of the tests to be performed in the hydrogen embrittlement program. Therefore, all thermal treatment of Ti-140A alloys was done at 1200°F followed by slow cooling to render them less susceptible to transformation embrittlement in subsequent tests. This reduced the possibility of having transformation embrittlement masking and confusing the results of hydrogen embrittlement. It is to be noted that the results shown in the figures are based on single specimen tests.

C. Since it is possible that much of the ductility losses encountered in alpha-beta alloys that have been exposed to stress and temperature is caused by hydrogen embrittlement and not by transformation embrittlement, the next step in this investigation was to investigate normally stable structures with and without hydrogen contamination. A heat of Ti-140A that contained 250 ppm was used in this phase of the program. Half of the bar stock was vacuum annealed at 1200°F for 24 hours and furnace cooled. The remaining half was given a comparable thermal history by annealing in a helium atmosphere. The hydrogen level remained at 250 ppm with the latter treatment while the vacuum anneal reduced the hydrogen level to 25 ppm. Specimens of both hydrogen levels were then exposed to various conditions of stress, time and temperature. These conditions, along with the percent reduction of areas that were obtained in subsequent room temperature fast tensile tests, are shown in Figure 4 and Figure 5.

In Figure 4 it is seen that as the conditions for creep embrittlement become increasingly severe there is a correspondingly greater loss in ductility for the hydrogen-contaminated specimens whereas the vacuum annealed material is affected very little, if at all. The data as presented here tend to indicate that much "creep embrittlement" encountered today is caused by the presence of hydrogen and not by transformation embrittlement.

III. DISCUSSION OF RESULTS

As can be seen by the data presented in this paper, hydrogen contaminated Ti-140A suffers embrittlement when exposed to stress, time and temperature. The embrittlement of the hydrogen-free material can be reduced to a negligible amount, however, by utilizing proper thermal treatments during fabrication or by employing a stabilizing treatment. Heating above 1200°F and rapid cooling results in a structure containing metastable beta that is susceptible to transformation embrittlement under subsequent service conditions. A slow cool after annealing at 1200°F allows the metastable beta to transform at temperatures above those at which embrittlement takes place and results in a structure of alpha and enriched beta that is stable under service conditions.

Of greater interest at this point is the embrittlement that takes place in the hydrogen contaminated specimens that had been "stabilized". As shown in Figures 4 and 5 the specimens containing hydrogen are embrittled under conditions that have very little effect, if any, on the vacuum annealed material. This brings up the question as to the mechanism involved. Of the various possibilities the following are listed for consideration:

1. Inherent hydrogen embrittlement wherein the mechanism is the same as that in the slow tensile and stress rupture tests.

2. Transformation embrittlement wherein decomposition of the beta phase is promoted by the presence of hydrogen or a hydride phase and which involves omega formation or coherency hardening.

3. Eutectoid embrittlement wherein decomposition of the beta phase is promoted by hydrogen or a hydride phase and which involves an embrittling dispersion of fine alpha and compound.

Of the above possibilities the most probable seems to be that of inherent hydrogen embrittlement by some unknown mechanism, perhaps similar to that encountered in steel. Work by Frost, et al(3) on the omega phase indicates that the presence of hydrogen does not affect the rate of omega formation. Their work, however, dealt with a very metastable beta phase produced by quenching from 1700°F, whereas this investigation deals with structures that were stabilized. The fact that stresses were involved in this work may also present a different problem. An investigation is underway to determine if the omega phase or a compound phase is present in the embrittled specimens. The absence of both would tend to support inherent hydrogen embrittlement by some mechanism independent of transformation embrittlement.

The fact that hydrogen is a beta stabilizing element does not lend any support to either (2) or (3) above. However, it is also thought that hydrogen has a tendency to expand the beta lattice. This may reduce the stabilizing effect under conditions of stress and temperature and promote the transformation to a pseudocubic structure.

The effect of stress in promoting embrittlement is not known. It appears to have an effect on the specimens in Figure 5. The difference in stress of 45,000 psi may strain the lattice in such a manner that much greater embrittlement occurs. At this time it appears that stress may be important from the standpoint of producing deformation, either elastic or permanent. A previous paper in this report dealt with the apparent dependence of hydrogen embrittlement on a deformed lattice.

IV. CONCLUSIONS

1. "Creep embrittlement" of slowly cooled material appears to be a result of hydrogen contamination rather than beta instability.

2. The ductility loss in hydrogen-free material when exposed to stress and temperature is caused by transformation embrittlement and can be controlled by proper thermal treatments.

3. It is suggested that hydrogen embrittlement and transformation embrittlement may be independent of each other. Additional work employing x-ray diffraction techniques should be undertaken to determine if hydrogen embrittlement in "stabilized" structures is accompanied by omega or compound formation.

4. The separate effects of stress, time and temperature should be evaluated for both transformation embrittlement and hydrogen embrittlement to aid in determining the mechanisms involved, and the relationship, if any, between them.

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(1) **WADC Technical Report 52-334, "Development of Titanium Base Alloys"**
(2) **See the testing methods section of this report**
(3) **WADC Technical Report 54-335 "Precipitation Hardening and Embrittlement in High Strength Titanium Alloys"**

DISCUSSION

Margolin: Was any metallographic work done in connection with the embrittled specimens? If so, did you observe any type of precipitate?

Wruck: Yes, we conducted a metallographic investigation along with the test program. However, no evidence of eutectoid, compound, hydride or any other precipitate was detected. We are presently employing X-ray diffraction techniques in an effort to establish the absence or presence of omega or compound in the brittle specimens.

Margolin: In an investigation of beta plasticity at New York University it was noted that the cube plane was normally the fracture plane. However, in some specimens fracture occurred along slip planes other than the cube plane. I suspect that some precipitation probably occurred in these instances.

Rostoker: You have investigated the effect of hydrogen on the tensile behavior of specimens after exposure to creep conditions. Have you investigated the effect of hydrogen on the creep behavior itself?

Wruck: No. We only attempted to control the amount of creep so as to obtain around 3 percent.

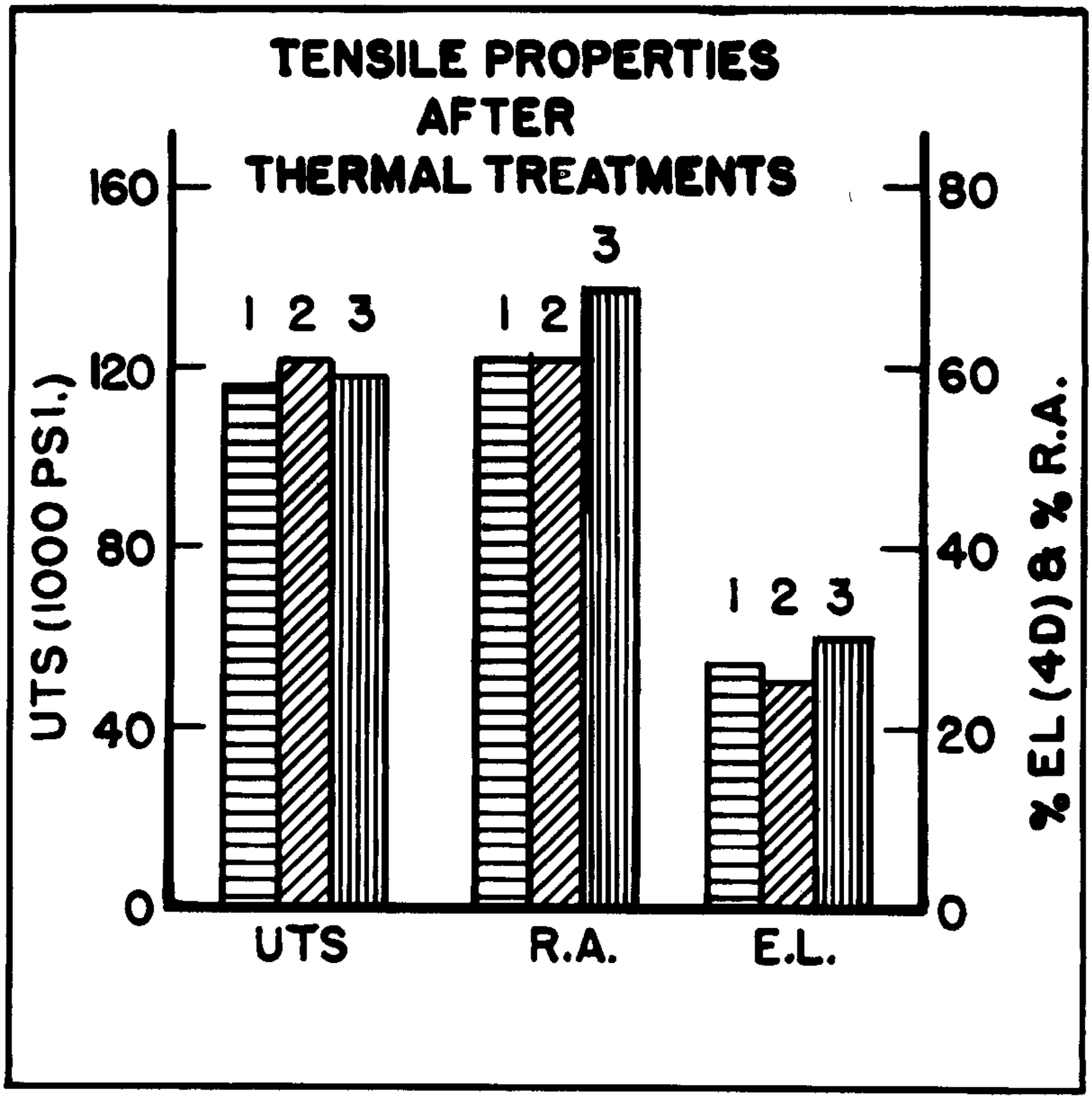
McClintick: At Mallory-Sharon Titanium, Inc., we investigated the creep embrittlement of alpha-beta alloys. The annealed, air-cooled material gave evidence of creep embrittlement whereas the quenched and aged material showed no evidence of creep embrittlement. This may put a brighter outlook on hydrogen as it appears that heat treatment increases the tolerance as far as creep embrittlement is concerned.

Wruck: What was the hydrogen level of the material?

McClintick: I do not know, but I imagine it was of the normal level present in commercial alloys.

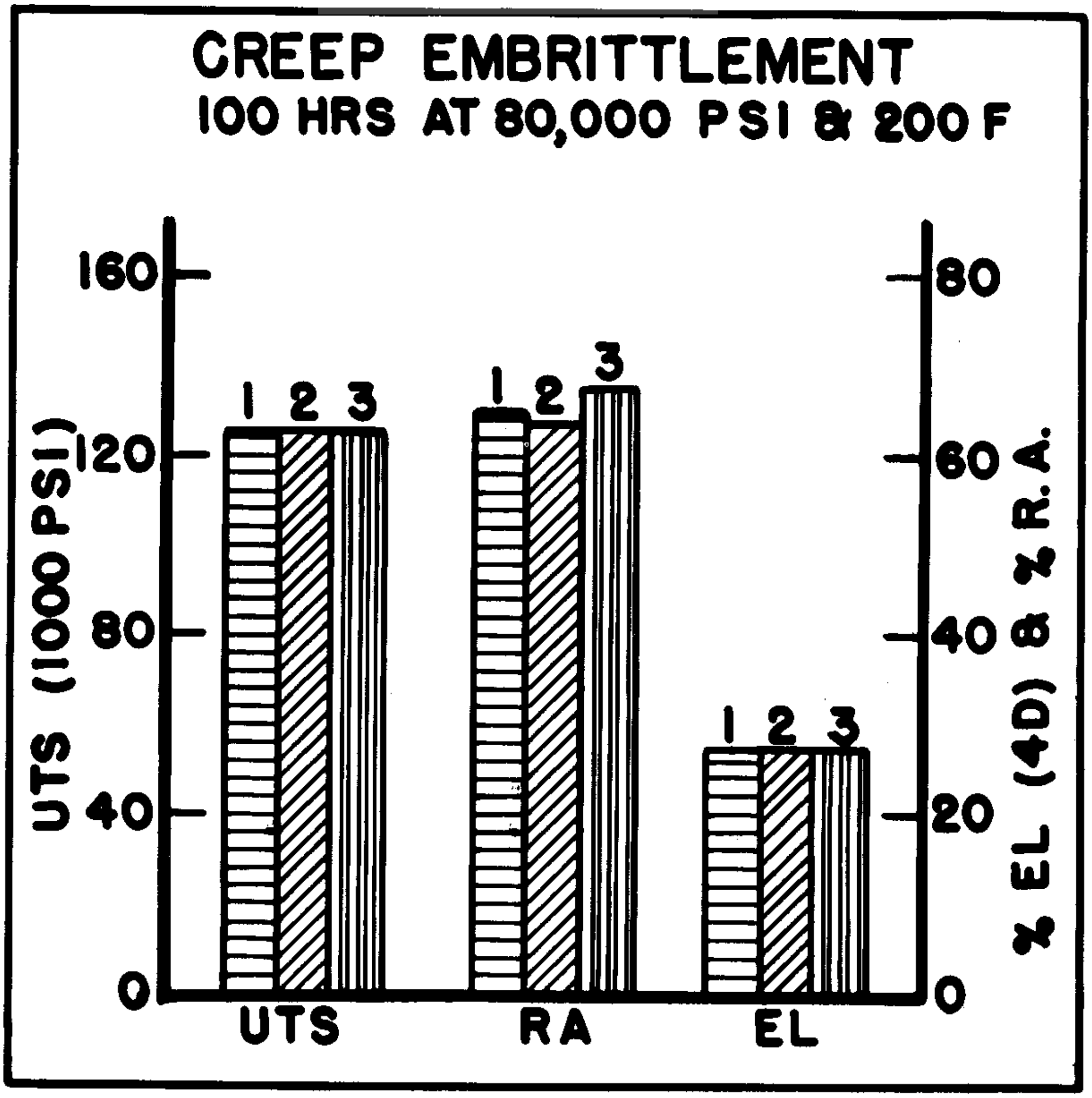
Wruck: You said the material was quenched and aged. At what temperature did you age and what were the subsequent creep embrittlement conditions?

McClintick: The alloy was aged at 1100°F. It was then exposed to 50,000 psi and 750°F for 300 hours.



Numbers above bars refer to thermal treatments
1 - Vacuum annealed at 1200°F for 24 hours; furnace cooled
2 - Vacuum annealed at 1200°F for 24 hours; air cooled
3 - Vacuum annealed at 1400°F for 24 hours; furnace cooled to 1200°F and air cooled

FIGURE 1. Room temperature tensile properties of Ti-140A after three thermal treatments



Numbers above bars refer to thermal treatments
1 - Vacuum annealed at 1200°F for 24 hours; furnace cooled
2 - Vacuum annealed at 1200°F for 24 hours; air cooled
3 - Vacuum annealed at 1400°F for 24 hours; furnace cooled to 1200°F and air cooled

FIGURE 2. Room temperature tensile properties of Ti-140A after exposure to embrittling conditions of 80,000 psi at 200°F for 100 hours

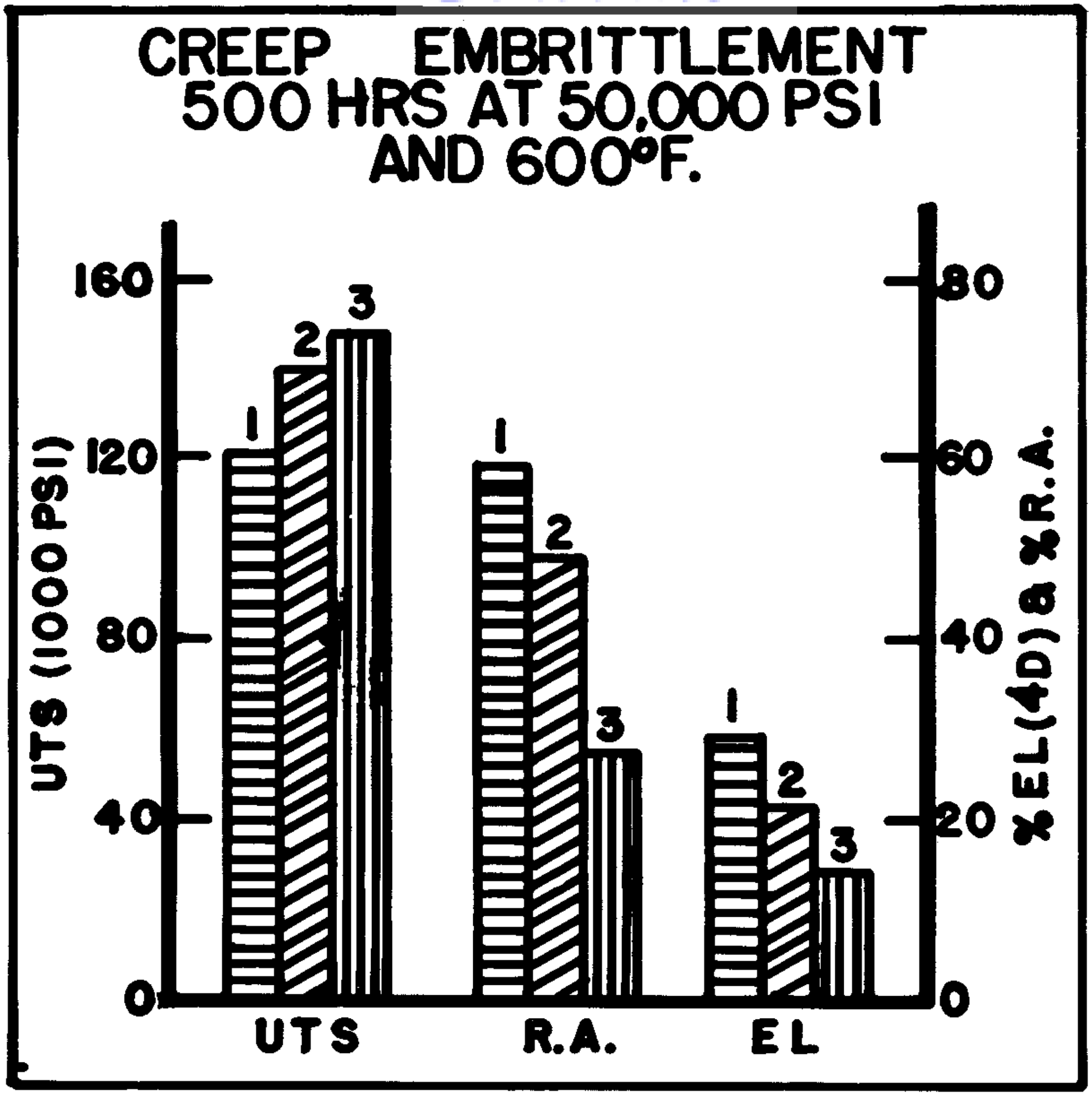
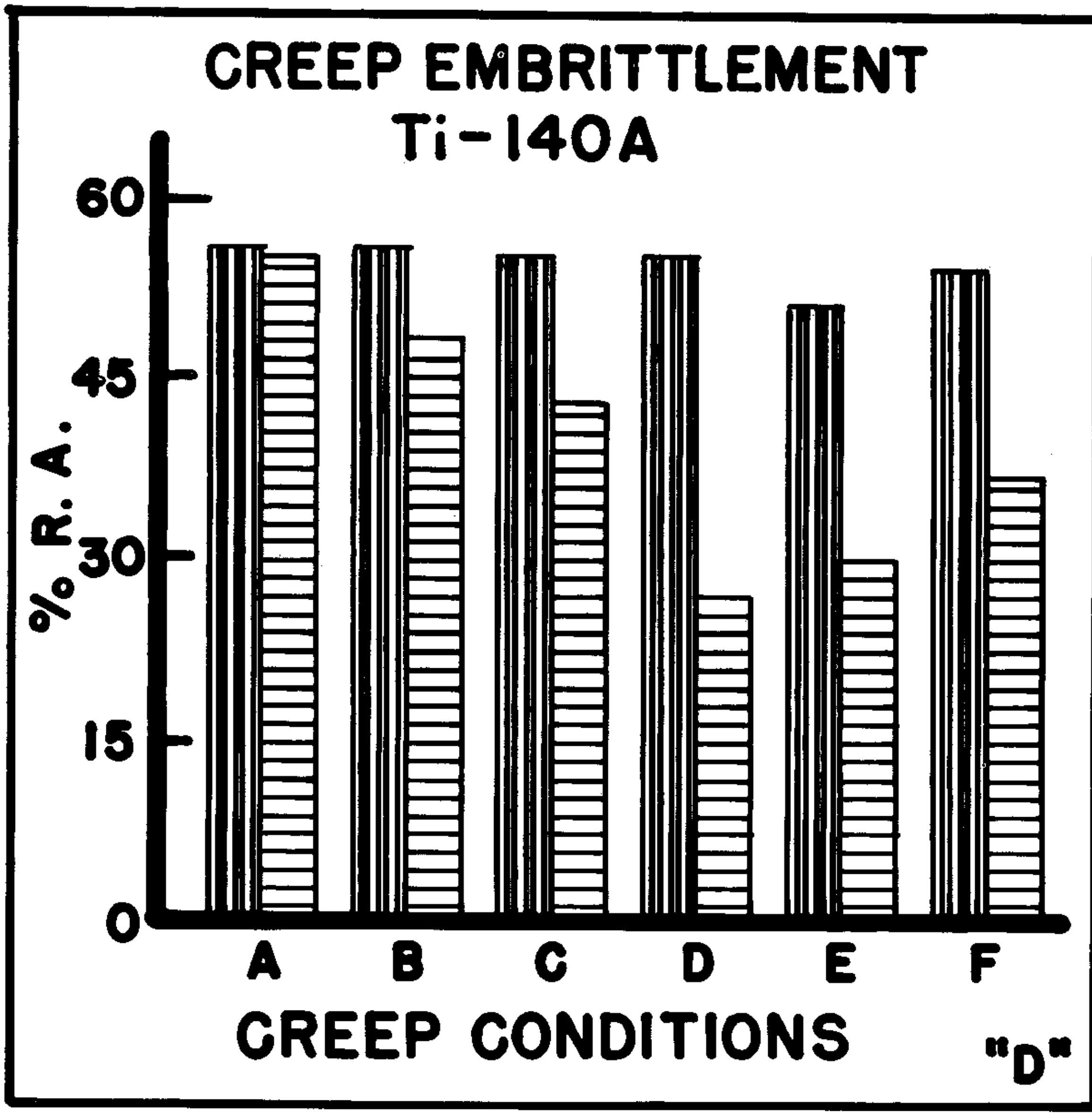


FIGURE 3. Room temperature tensile properties of Ti-140A after exposure to embrittling conditions of 50,000 psi at 600°F for 500 hours

Numbers above bars refer to thermal treatments
1 - Vacuum annealed at 1200°F for 24 hours; furnace cooled
2 - Vacuum annealed at 1200°F for 24 hours; air cooled
3 - Vacuum annealed at 1400°F for 24 hours; furnace cooled to 1200°F and air cooled

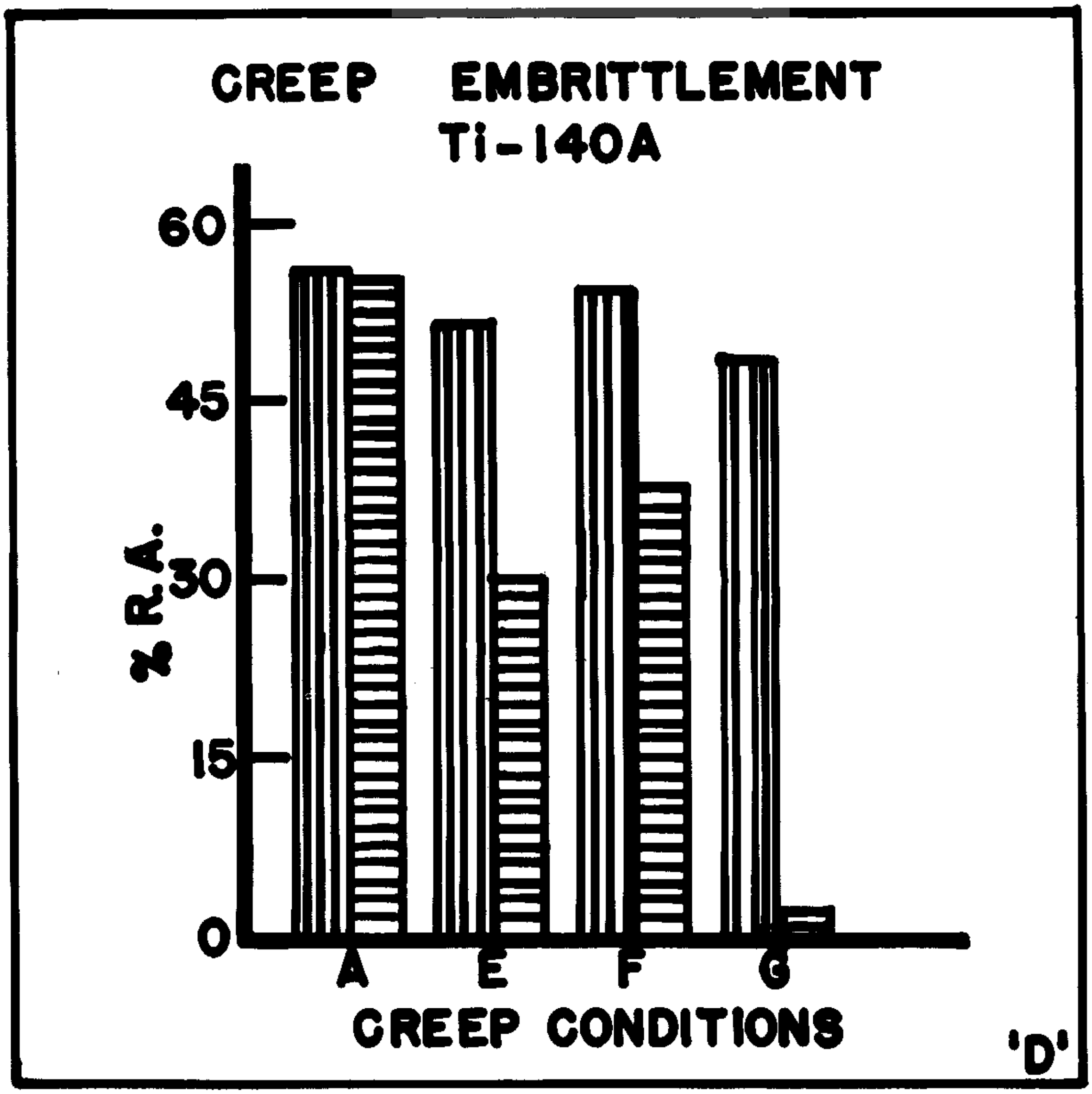


Vertical bars represent Ti-140A with 25 ppm hydrogen
Horizontal bars represent Ti-140A with 250 ppm hydrogen

Creep Conditions

A - As thermally treated, no exposure to embrittling conditions
B - Exposed to 95,000 psi at room temperature for 500 hours
C - Exposed to 80,000 psi at 200°F for 100 hours
D - Exposed to 80,000 psi at 200°F for 500 hours
E - Exposed to 50,000 psi at 600°F for 100 hours
F - Exposed to 50,000 psi at 600°F for 500 hours

FIGURE 4. Reductions in area obtained in room temperature tensile tests for Ti-140A of two hydrogen levels



Vertical bars represent Ti-140A with 25 ppm hydrogen
Horizontal bars represent Ti-140A with 250 ppm hydrogen

Creep Conditions

A - As thermally treated, no exposure to embrittling conditions
B - Exposed to 50,000 psi at 600°F for 100 hours
F - Exposed to 50,000 psi at 600°F for 500 hours
G - Exposed to 95,000 psi at 600°F for 1000 hours

FIGURE 5. Reductions in area obtained in room temperature tensile tests for Ti-140A of two hydrogen levels

THE EFFECTS OF HYDROGEN ON THE MECHANICAL PROPERTIES OF TITANIUM

by

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Battelle Memorial Institute

Introduction

The purpose of this paper is to summarize the work done at Battelle Memorial Institute, under the sponsorship of Watertown Arsenal, on "The Effect of Hydrogen on the Mechanical Properties of Titanium and Titanium Alloys". This work has been in progress since mid-1951, and was the first to point out the dangers of hydrogen embrittlement of alpha and alpha-beta alloys. A number of technical reports(1,2,3,4) and papers(5,6,7) have been published or are ready for publication. This paper will summarize some of the effects of hydrogen on the alloys themselves. Other parts of the investigation have been concerned with the control of hydrogen in processing of titanium and its alloys, and are not to be included.

It also is an objective of the paper to emphasize that sufficient hydrogen will embrittle titanium alloys under any conditions of testing. There is no "safe" condition in which hydrogen embrittlement does not occur. The chief concern is to determine those conditions of testing in which embrittlement occurs with the least hydrogen content.

Tests used in studying the effects of hydrogen were unnotched and notched ($K_T = 3$) tensile tests usually at 0.005 inch per minute, and a notch-bend impact test. The impact test was performed on a micro specimen(8). In this test, the energy absorption in inch-pounds correlates fairly well with Charpy foot-pounds for the same material tested as a standard V-notch Charpy.

Alpha Alloys

The beta-stabilizing nature of hydrogen in titanium is shown in McQuillan's diagram[8], shown in Figure 1. The dependence of concentration of hydrogen on pressure is shown by the isobars thereon. Solubility of hydrogen in alpha is a maximum at the eutectoid temperature, but decreases rapidly at lower temperatures, as is shown in Figure 2 for high-purity titanium[6]. Since commercial titanium usually contains some retained beta as a result of iron contamination, the solubility of hydrogen in commercial titanium is somewhat greater than in high-purity titanium, because hydrogen has to saturate the beta phase as well as the alpha before hydride precipitates. Titanium hydride precipitates from alpha titanium in characteristic plate-like form when slowly cooled, as illustrated in Figure 3A, and in a characteristic finely dispersed "salt and pepper" fashion when quenched from the alpha field, as shown in Figure 3B. Commercial-purity titanium containing 0.3 per cent iron and 220 ppm hydrogen (cf. Figure 4) has a structure consisting of alpha plus retained beta plus hydride plates when slowly cooled.

Iodide Titanium

The effect of hydrogen on the unnotched tensile properties at room temperature is shown in Figure 5. Under these conditions, brittleness does not set in until over 30 atom per cent (9000 ppm) hydrogen is present. This is a quite high content of hydrogen. With contamination levels for hydrogen up to about 200 ppm, there is no significant effect at all on unnotched tensile properties at room temperature.

Under notch-bend impact conditions, hydrogen is much more damaging to ductility. Substantial losses of toughness occur with as little as 50 ppm hydrogen, and complete loss of toughness occurs with 300-400 ppm hydrogen. Some improvement in the toughness of iodide titanium containing hydrogen can be made by quenching from the alpha field(6). However, the improvement is not permanent, and decays with time, as is shown in Figure 6.

The tensile properties of iodide titanium containing up to 400 ppm hydrogen were studied at various temperatures from -196 to 100 C, at three testing speeds from 0.005 inch per minute to 18.1 feet per second, with and without a notch of $K_T = 3$. Increased strain rate, decreased testing temperature, or the presence of a notch generally tended to increase strength and lower ductility for any given hydrogen content. The reduction-in-area values for the unnotched samples at the three testing speeds are shown in Figure 7. Iodide titanium substantially free of hydrogen is seen to have high ductility under any of the testing conditions. For any given testing speed, the ductilities drop off at progressively higher temperatures as the hydrogen content increases. As the testing speed is increased, the drop-off occurs at higher temperatures. The reduction-in-area values of the notched high-purity titanium-hydrogen alloys are shown in Figure 8. The temperatures of transition from ductile to brittle values of reduction in area are seen to be higher for the notched material, other factors being equal.

The poor notch-bend impact characteristics of the iodide titanium-hydrogen alloys are the result of an adverse effect of hydrogen on both strain-rate and notch sensitivity. Thus, the condition in which the least hydrogen is required to result in brittle behavior appears to be for notched specimens at impact speeds. However, even with unnotched specimens, serious low-temperature embrittlement is noted with relatively small amounts of hydrogen well within the impurity levels encountered in commercial practice.

Commercial-Purity Titanium

The effect of hydrogen on the unnotched tensile properties of commercial titanium at room temperature is shown in Figure 9. The amount of hydrogen resulting in loss of ductility is seen to be about 10 atom per cent (about 2200 ppm), which is somewhat less than that of high-purity titanium, but still is a quite high content. Almost complete loss of notch impact toughness of commercial titanium occurs with much lower hydrogen contents, above about 200 ppm. The effect of cooling rate and subsequent storage at room temperature on the notch-bend impact properties is shown in Figure 10. This shows that, although there is a substantial increase in the toughness as a result of quenching from the alpha field, this decays with time until it is substantially the same as that of slow-cooled samples. The effects of hydrogen content, testing speed, testing temperature, and the presence of notches were checked in the same way as for the high-purity base.

The effect of strain rate on the ductility of unnotched specimens, shown in Figure 11, is somewhat surprising. At 25 C, impact speeds are embrittling for the high-hydrogen material, while at -196 C, impact speeds result in higher ductility. In any event, the effect of strain rate on the ductility of commercial-base titanium-hydrogen is not nearly so important as the presence of a notch. Commercial titanium is relatively notch sensitive as a result of its interstitial content. Hydrogen makes it even more notch sensitive. This factor dominates the behavior of commercial titanium containing hydrogen, so much that strain-rate effects are masked. Slow and impact notch-bend tests give about the same energy absorption over a range of testing temperatures. Notched tensile specimens tested at slow, fast, or impact speeds also exhibit about the same ductility under the notch. Figure 12 shows the tensile ductility as a function of temperature of notched and unnotched specimens of commercial-base titanium-hydrogen.

Titanium-Aluminum and Titanium-Nitrogen

A brief study was made of the hydrogen embrittlement of high-purity titanium-aluminum and titanium-nitrogen alloys characterizing substitutional and interstitial solutes(6). It was found that the tensile properties were substantially unaffected by about 130 ppm hydrogen, but that the notch-bend impact properties were severely lowered. This is in substantial agreement with the other results on all-alpha alloys.

Alpha-Beta Alloys

Since hydrogen is a beta stabilizer, as shown in Figure 1, it partitions preferentially to the beta phase in an alpha-beta alloy. The partition in pure titanium is about 5:1 at the eutectoid temperature, below which beta decomposes into alpha and gamma. The partition to beta is even greater in alpha-beta alloys at room temperature, since the alpha solubility of hydrogen decreases to practically nil at room temperature.

A number of alpha-beta alloys were studied. In particular, a detailed study was made of the commercial Ti-8Mn alloy (C-110M), covering the effects of testing speed, testing temperature, the presence of notches, and hydrogen content.

None of the alpha-beta alloys studied exhibited a hydride phase metallographically, although hydrogen contents of up to 1000 ppm were investigated.

C-110M Alloy

The effects of hydrogen on the unnotched slow tensile properties at room temperature of the commercial Ti-8Mn alloy are shown in Figure 13. There is a very sharp decrease in tensile ductility at about 200 ppm hydrogen. Notch-bend impact properties were decreased only slightly with up to 1200 ppm hydrogen.

Testing temperature has a most important effect on ductility in the tensile test, as is shown in Figure 14. As the testing temperature is reduced, the maximum hydrogen content at which good ductility is found becomes lowered to well below 200 ppm. If the temperature is increased to 100 C, the alloy will exhibit excellent ductility with 600 ppm hydrogen. This suggests that hydrogen tolerance (in slow tensile tests, at any rate) varies with the testing temperature. Increasing testing speed overcomes the loss in ductility to some extent, as shown in Figure 15. However, it is important to bear in mind that if sufficient hydrogen is present, or the temperature lowered sufficiently, brittle behavior will result at the highest strain rate. Thus, Figure 15 shows that even at impact speed, C-110M with 500-1000 ppm hydrogen is brittle at -40 C. The presence of a notch increases strength but is embrittling to the 8 per cent manganese alloy even without hydrogen present. This may be viewed as an effect of a notch in raising a ductile-brittle transition temperature. Furthermore, as is shown in Figure 16, the temperature at which reduction in area under the notch begins to increase is greater for the alloy with 200 ppm hydrogen than with 10 ppm. This is the same thing as saying that both hydrogen and notches increase the ductile-brittle transition temperature.

Other Alpha-Beta Alloys

The test in which brittle behavior in alpha-beta alloys was found with the least hydrogen content was the 0.005-inch-per-minute tensile test (rupture tests were not conducted). High-purity Ti-3Mn, Ti-6Mn, Ti-5Mo, and Ti-11Mo alloys were studied in the alpha-beta condition. Also, the C-130AM commercial alpha-beta alloy containing 4 per cent aluminum and 4 per cent manganese was evaluated. The results of the slow tensile tests on these alloys over a range of hydrogen contents are shown in Figure 17. The high-purity manganese alloys become embrittled at about 200 ppm hydrogen, the 4Al-4Mn alloy will withstand about 1000 ppm hydrogen before embrittlement, and the titanium-molybdenum alloys will withstand hydrogen with up to about 700 ppm without exhibiting brittleness in the slow tensile test. Generally, notch-bend impact tests were much less affected by hydrogen. The fact that the high-purity titanium-manganese alloys were embrittled by the 200 ppm hydrogen content the same as the commercial 8 per cent manganese alloy, would seem to indicate that interstitial level does not have much effect. However, such a conclusion would need more verification, because the opposite would be expected. The 11 per cent molybdenum alpha-beta alloy, although not becoming completely brittle, did show considerable loss of reduction in area in a slow test but not in a fast test, indicating a definite effect of hydrogen on reducing ductility. The relatively high tolerance in slow tension for the 4Al-4Mn alloy, compared with the binary titanium-manganese alloys, suggests that alpha-stabilizing aluminum has a beneficial effect.

All-Beta Alloys

So far, only a relatively small number of all-beta alloys have been evaluated for effects of hydrogen. In the present work, high-purity Ti-9Mn, Ti-13Mo, and Ti-20Mo alloys have been checked. The Ti-9Mn alloy, quenched from the beta field, was studied with up to about 700 ppm hydrogen in slow tensile tests and notch-bend impact tests. The tensile strength was lowered slightly, but the tensile ductility and notch-bend impact properties were unaffected by this much hydrogen, as shown in Figure 17.

The two high-purity titanium-molybdenum beta alloys, as quenched from the beta field, were tested with up to about 2000 ppm hydrogen. Even with this much hydrogen, there was no indication of a second phase. The mechanical properties of the Ti-13Mo alloy are summarized in Figure 18. Tests were conducted for unnotched and notched specimens with $K_T = 3$ at slow, 0.005 inch per minute, and fast, 0.5 inch per minute, testing speeds. The only noticeable effect is a slight decrease in strength and an increase in ductility, particularly with the notched specimens. The results for the Ti-20Mo beta alloy were substantially the same as for the 13 per cent molybdenum alloy, and are not reproduced here. Notch-bend impact properties of the titanium-molybdenum alloys were somewhat at variance, in that the notch-bend impact transition temperature for the 13 per cent molybdenum alloy was increased by hydrogen, while there was no effect on the 20 per cent molybdenum alloy. Even with high concentrations of hydrogen present, however, the notch toughness of the titanium-molybdenum alloys was quite good.

Data on the effects of hydrogen on three alloys certainly are not sufficient basis to justify a broad conclusion. However, it seems apparent that the effect of hydrogen on titanium alloys in the all-beta condition is not very deleterious.

Discussion

As stated at the outset of this paper, one of the objectives of the work done was to determine those testing conditions in which brittle behavior would be found with the least hydrogen content. For the alpha alloys, this generally corresponded to testing notched specimens at high strain rates, a set of conditions which one normally would associate with the greatest tendency toward brittle behavior. For the alloys tested in the all-beta condition, hydrogen embrittlement was not noted up to relatively high hydrogen contents in slow tension. However, there generally was an increase in the ductile-brittle transition for notch-bend impact tests, this, again, being normal expected behavior. For the alpha-beta alloys, hydrogen embrittlement was first noted in slow tension. At the same time, there was only a relatively small effect on notch-bend impact characteristics. This behavior suggests that hydrogen embrittlement of alpha-beta alloys occurs by a strain-aging mechanism. Further, slower strain rates would be expected to result in embrittlement at lower hydrogen contents. This has been very convincingly demonstrated by the rupture tests conducted by WADC. However, the amount of hydrogen required to embrittle an alpha-beta titanium alloy in slow tension decreases as the testing temperature decreases. This suggests that embrittlement may occur at even lower hydrogen contents than are found in room-temperature rupture tests.

At this early stage in the hydrogen problem, it is best to view hydrogen embrittlement of titanium alloys as only one of many possible ways to embrittle the material. For example, if an alloy is so notch sensitive as a result of high oxygen that it behaves brittlely in a notch tensile test at room temperature, there is no way to set up a specification for hydrogen tolerance based on good notch ductility. Considering notched tensile strength, for both the all-alpha and all-beta materials, it has been observed that hydrogen eventually will decrease notched tensile strength to values below that of the unnotched tensile strength. However, considerably more hydrogen is required to do this than to reduce the notch ductility to values usually considered brittle. The amount of hydrogen that any material can tolerate will depend to a large extent on the degree of brittleness tolerable for the particular application. This will, of course, vary from case to case and from alloy to alloy. Any quality consideration should weigh hydrogen as one of the embrittling factors to guard against. A good policy to gain the greatest tolerance for hydrogen would appear to be to reduce the other embrittling factors to a minimum. Lastly, of course, hydrogen contents should be kept to a minimum through proper control of sponge quality and processing steps.

Acknowledgment

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DISCUSSION

Wayman: It has been suggested that precipitation of a hydride phase may cause the embrittlement. I question this, since in steel, where hydrogen embrittlement also occurs, there is no evidence for precipitation of a hydride phase.

Jaffee: According to present day thinking it is not necessary to have a visible precipitate in order to have embrittlement. The Cottrell mechanism involving diffusion of solute elements to dislocations could cause embrittlement. It is equally feasible to postulate other mechanisms. I think the final answer will be that the hydrogen embrittlement of an alpha-beta alloy involves many processes.

The fact that some investigators have shown a partial recovery of ductility as the test temperature decreases, and that others have not, would indicate that in most cases there is a net loss in ductility at low test temperatures. Any restoration of ductility that occurs, due perhaps to low rates of diffusion, is only part of the story. I suspect, that in addition to the strain aging effect, high contents of hydrogen in beta can cause a normal solid solution embrittlement at low temperatures.

Wayman: What is the status of identification of the precipitates in alpha and alpha-beta alloys?

Jaffee: I showed a photomicrograph for an alpha-beta alloy containing 450 ppm hydrogen. There was a precipitate between the alpha particles in the beta matrix; we don't yet know what this precipitate is. In all-alpha alloys, however, the phase present is clearly titanium hydride.

Anonymous: Do you have any idea why aluminum additions should increase the hydrogen tolerance of an alpha-beta alloy?

Jaffee: No.

Kessler: With reference to the photomicrograph you showed of Ti-140A, is it not generally true that alpha-beta alloys in general, and Ti-140A in this case, will show a precipitate when the hydrogen content is high, even at the 450 ppm level?

Jaffee: Apparently the material must be deformed in order to obtain the precipitate at this hydrogen level.

Kessler: We have not seen this precipitate even under conditions of deformation. For the past 6 months we have been running notch tensile tests and other types of tests under stress. We have never been able to produce the precipitate, even in the area of the notch, or in samples that failed in standard tensile tests after long time exposure near the fracture.

Jaffee: Have you not seen the structure in Ti-150A?

Kessler: No, we have not been able to reproduce it. I think that with Ti-150A, the dark etching phase present in some of the failures is associated with exposure to temperature and stress; the thermal cycle is important.

Jaffee: It is quite elusive, it took us a long time to find the precipitate.

Kessler: In your last slide you used hydrogen tolerance while discussing the manganese and molybdenum alloys. Hydrogen tolerance is a rather poorly defined thing. It depends upon the test that you use, and I don't think that you can use the term "tolerance" when you talk about the slow speed tensile test.

Jaffee: I explained that the amount of hydrogen necessary to cause brittle behavior will depend upon the test being used. The "tolerance" is defined with respect to a particular test.

Kessler: I would like to make one further comment. All of this mechanical property test work has been directed towards determining the hydrogen limits that are permissible in the various alloys. Some of these tests are quite complicated, and simple hydrogen analysis methods are available. I feel that once we have determined these hydrogen limits, the analysis methods will be much more useful and exact.

Hahn: Would you elaborate on the results which you obtained with the all-beta materials?

Jaffee: Our limited experience has been with three high-purity beta-quenched alloys, one alloy with manganese, and two with molybdenum. For these materials, the slow speed tensile test has shown no evidence for embrittlement up to quite high hydrogen levels. However, notch bend impact tests over a range of temperatures, indicate that the higher the hydrogen level the higher is the notch impact transition temperature. All-beta alloys apparently behave like all-alpha material. Thus the all-alpha and all-beta materials show similiar behavior in mechanical property tests, namely; excellent ductility in slow speed tensile tests and susceptibility to embrittlement in notch bend impact tests over a range of temperatures. Alpha-beta alloys exhibit the strain aging type of embrittlement.

Margolin: Were the 3 manganese and the 6 manganese alloys heat treated at the same temperatures? I noticed that there was a difference in their reductions in area, and wondered if this could be ascribed to a difference in the amount of alpha-beta interface.

Jaffee: Both alpha-beta Ti-Mn alloys were tested as quenched from 750°C. We had expected that the greater the amount of beta of the same composition, the more hydrogen would be required for embrittlement and the greater would be the total degree of embrittlement. Because of the solubility relationships, we expected to find with an all-beta alloy the highest level of hydrogen needed for embrittlement, yet the greatest degree of embrittlement. However the experiment did not bear this out. Both alloys were embrittled by about the same amount of hydrogen. There is more interface in the 3%

alloy than in the 6% alloy, but I don't think that there are enough data for a generalization. You would probably be more correct reasoning logically, than trying to analyze these particular tests. I think the important thing is that the tolerance was substantially the same as that for the commercial 3% manganese, alpha-beta alloy.

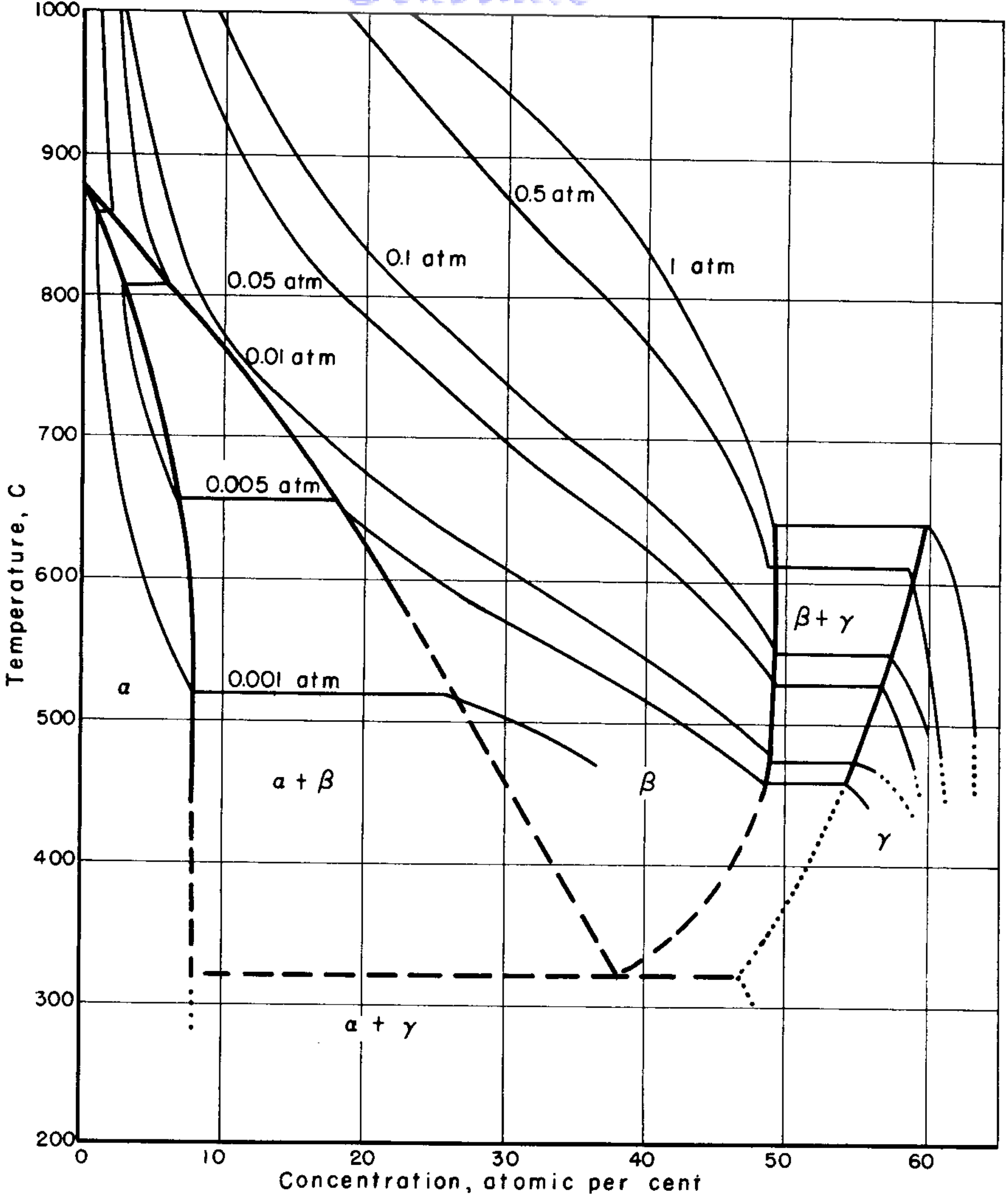


FIGURE 1 CONSTITUTIONAL DIAGRAM FOR IODIDE TITANIUM-HYDROGEN SYSTEM

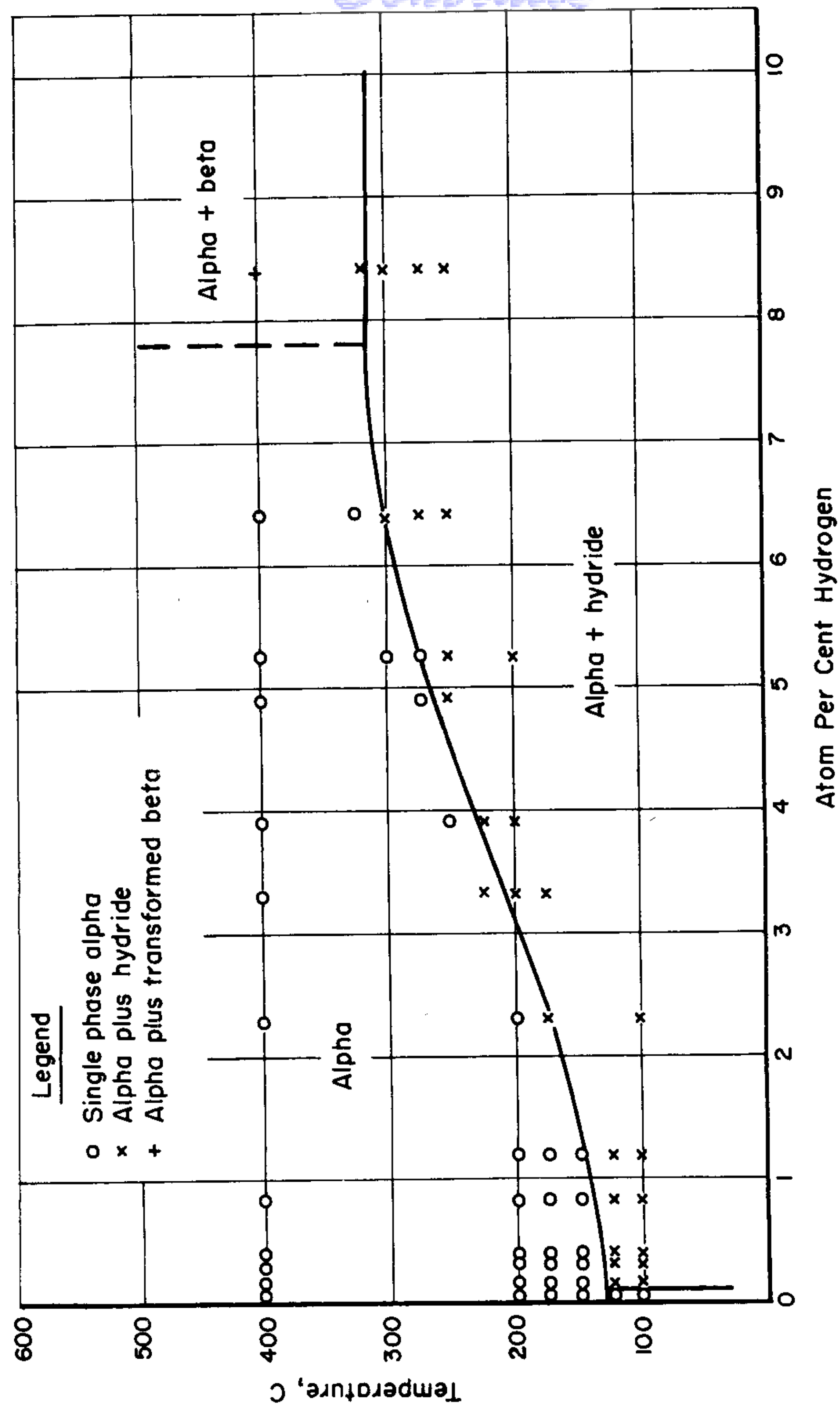
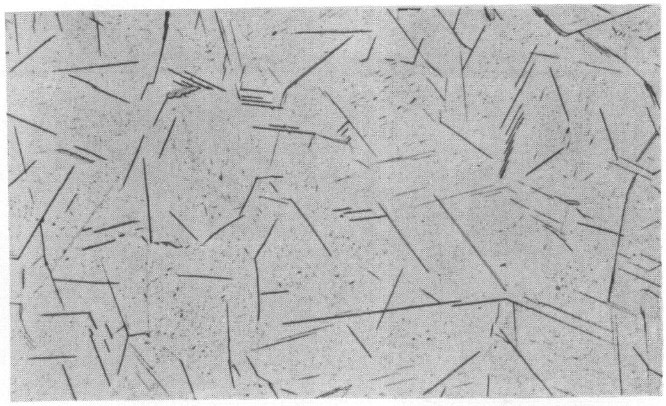


FIGURE 2. LOW-TEMPERATURE ALPHA-SOLUBILITY LIMIT FOR HYDROGEN IN HIGH-PURITY TITANIUM



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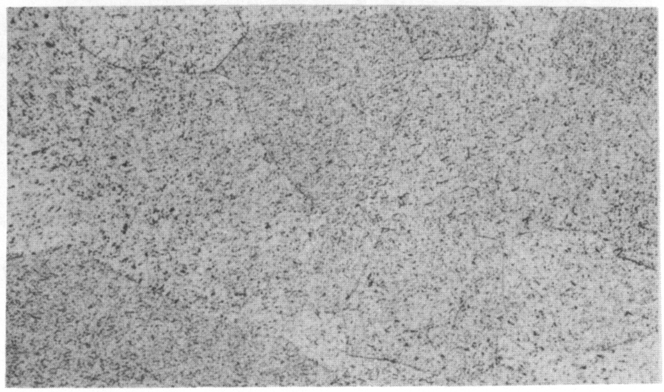

B

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FIGURE 3. IODIDE TITANIUM WITH 240 PPM HYDROGEN; (A) SLOWLY COOLED FROM 350 C, THROUGH HYDRIDE PRECIPITATION REGION, (B) QUENCHED FROM 250 C

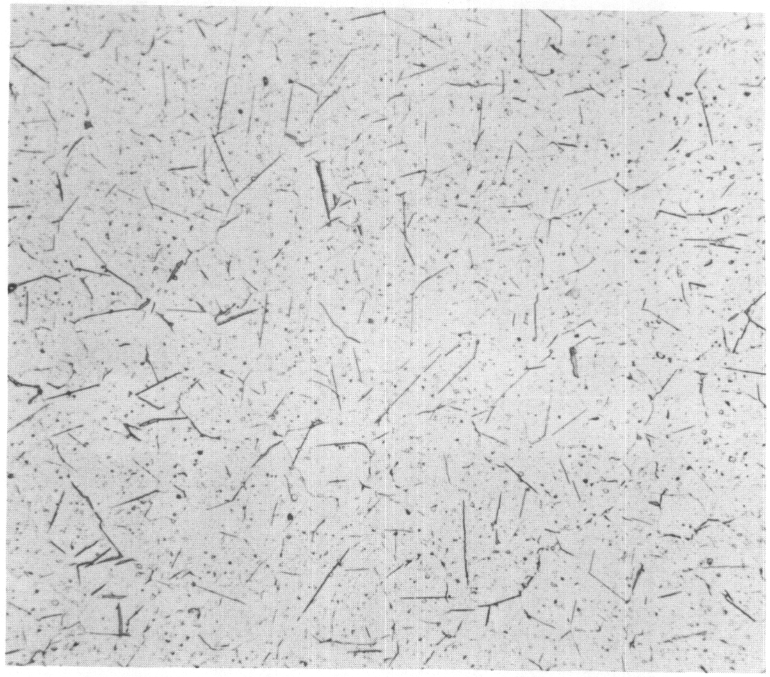

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FIGURE 4. COMMERCIAL-PURITY TITANIUM, WITH 0.3 PER CENT IRON AND 220 PPM HYDROGEN, SLOWLY COOLED FROM 400 C THROUGH HYDRIDE PRECIPITATION REGION

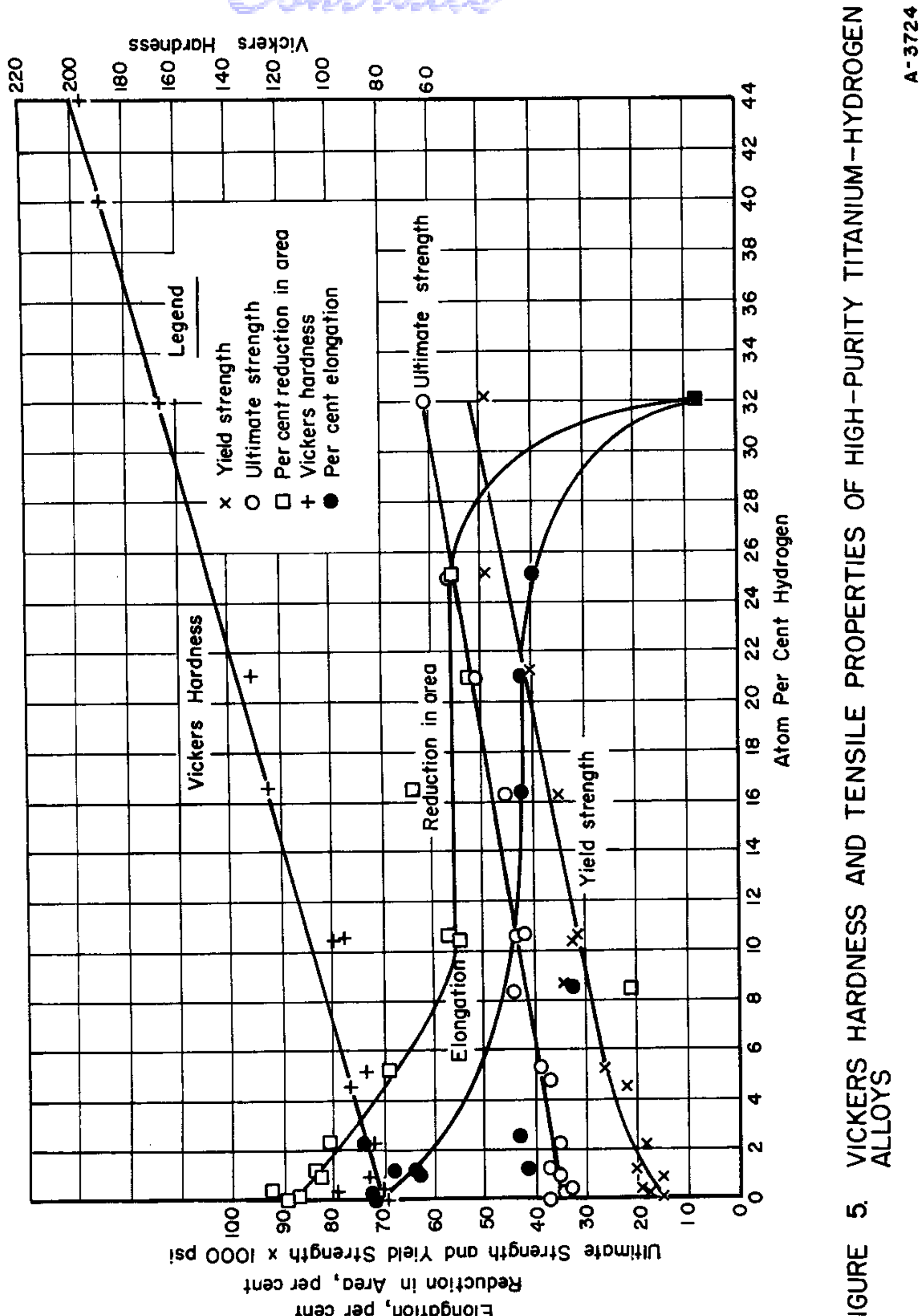

FIGURE 5. VICKERS HARDNESS AND TENSILE PROPERTIES OF HIGH-PURITY TITANIUM-HYDROGEN ALLOYS

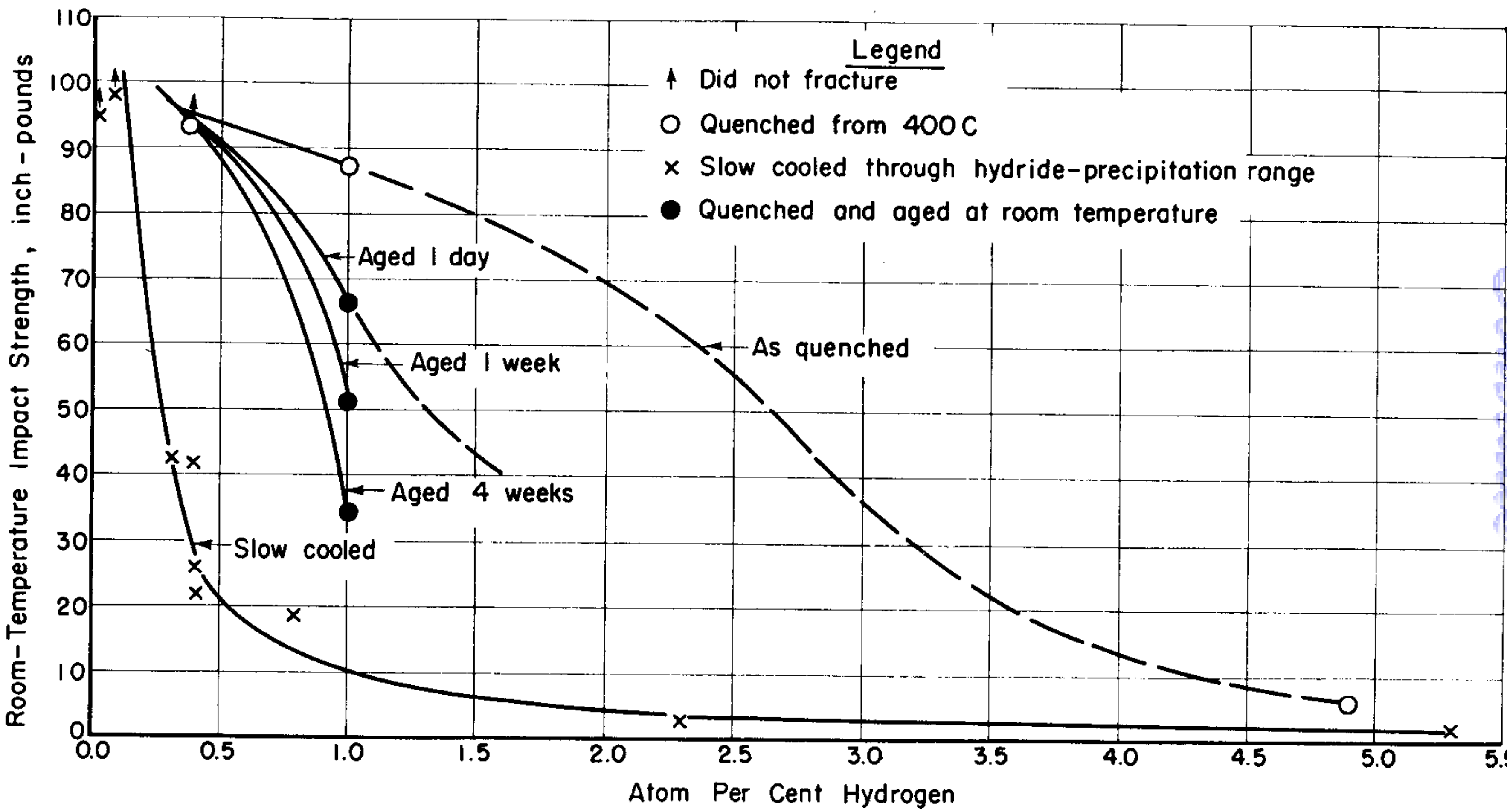

FIGURE 6. BENEFICIAL EFFECT ON TOUGHNESS OF WATER QUENCHING FROM ALPHA-PHASE FIELD AND TOUGHNESS DECAY ON ROOM-TEMPERATURE AGING

A-3720

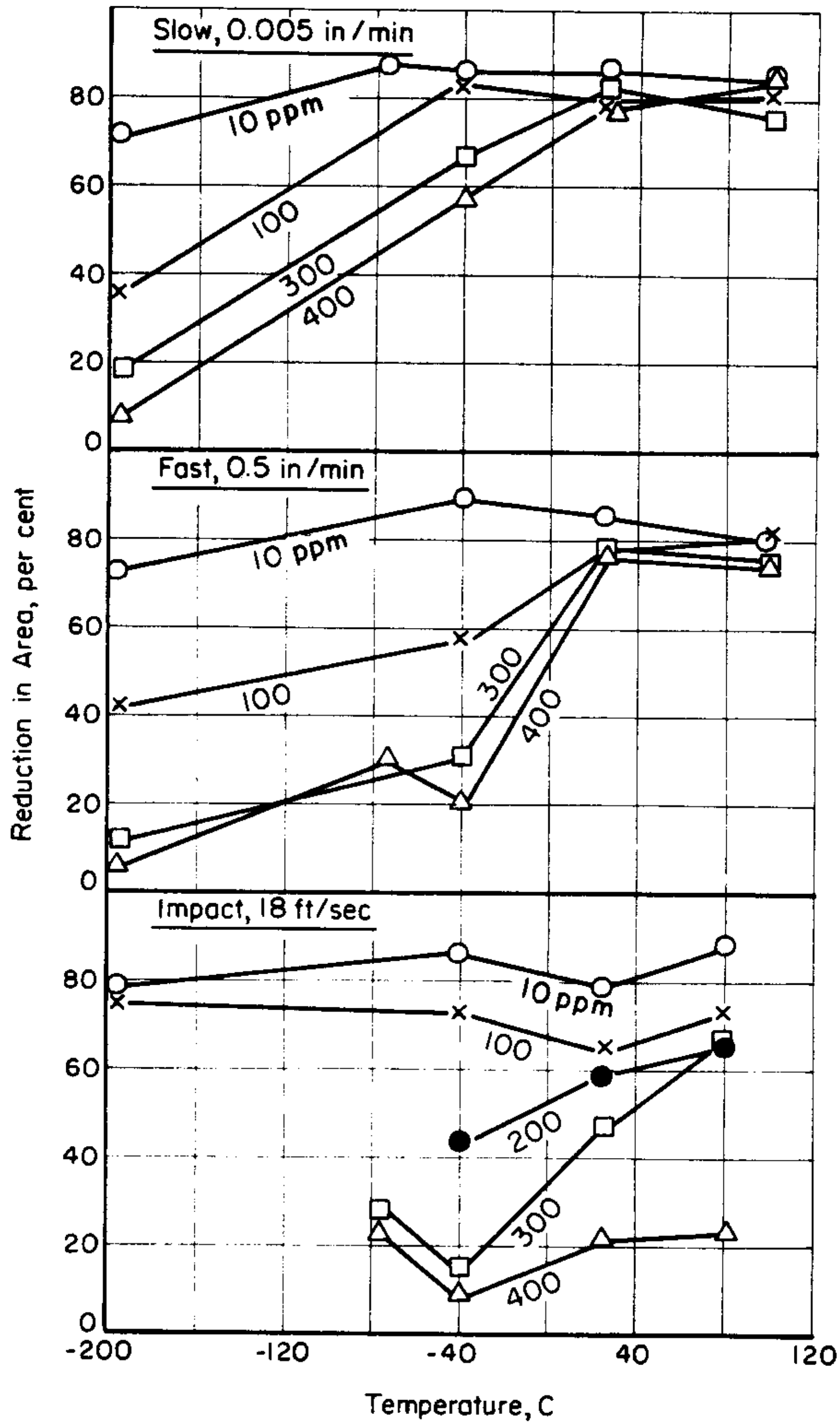

FIGURE 7. DUCTILITY OF UNNOTCHED HIGH-PURITY Ti-H ALLOYS IN TENSION AT THREE TESTING SPEEDS

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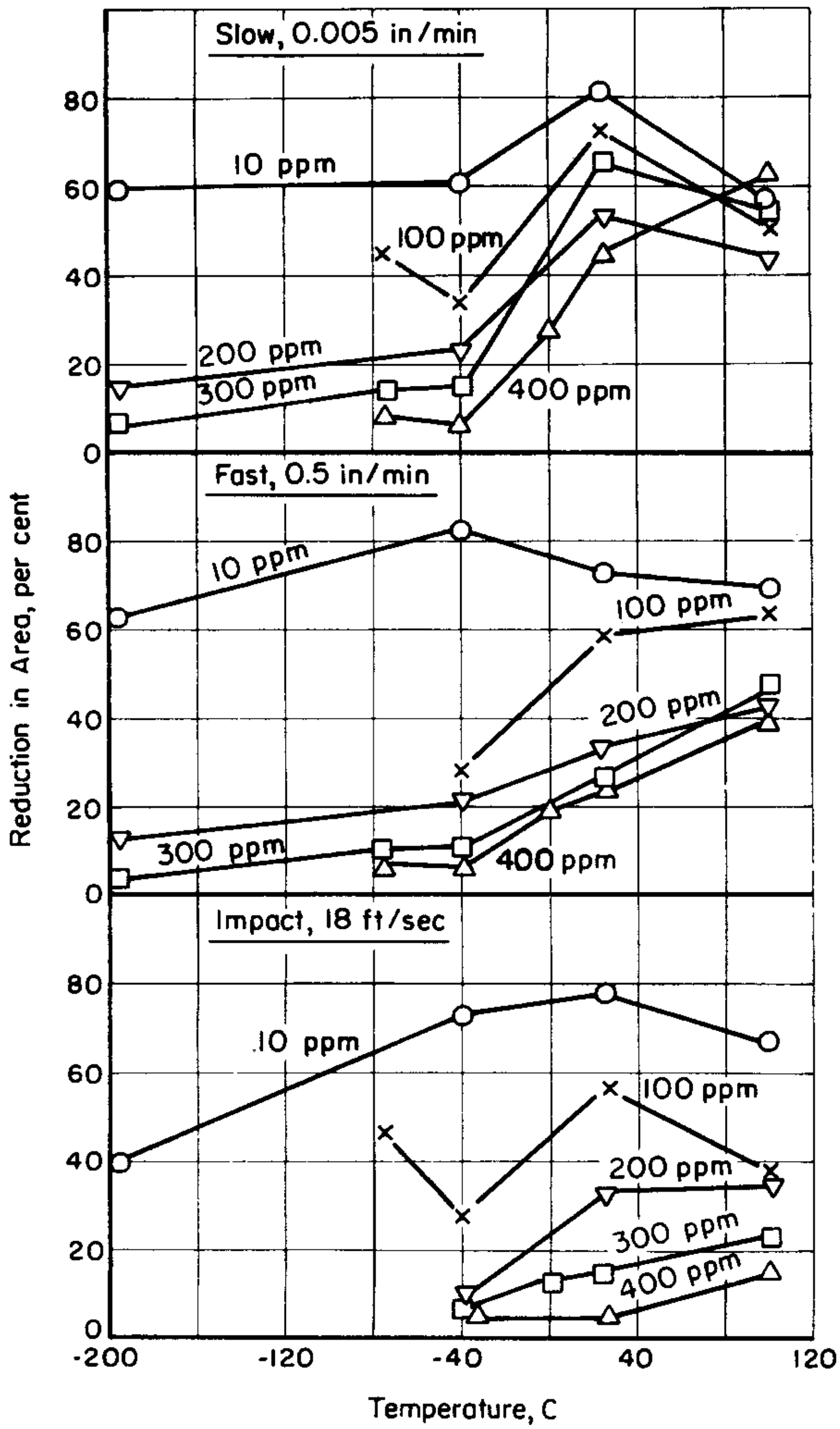

FIGURE 8. DUCTILITY OF NOTCHED HIGH-PURITY Ti-H ALLOYS IN TENSION AT THREE TESTING SPEEDS

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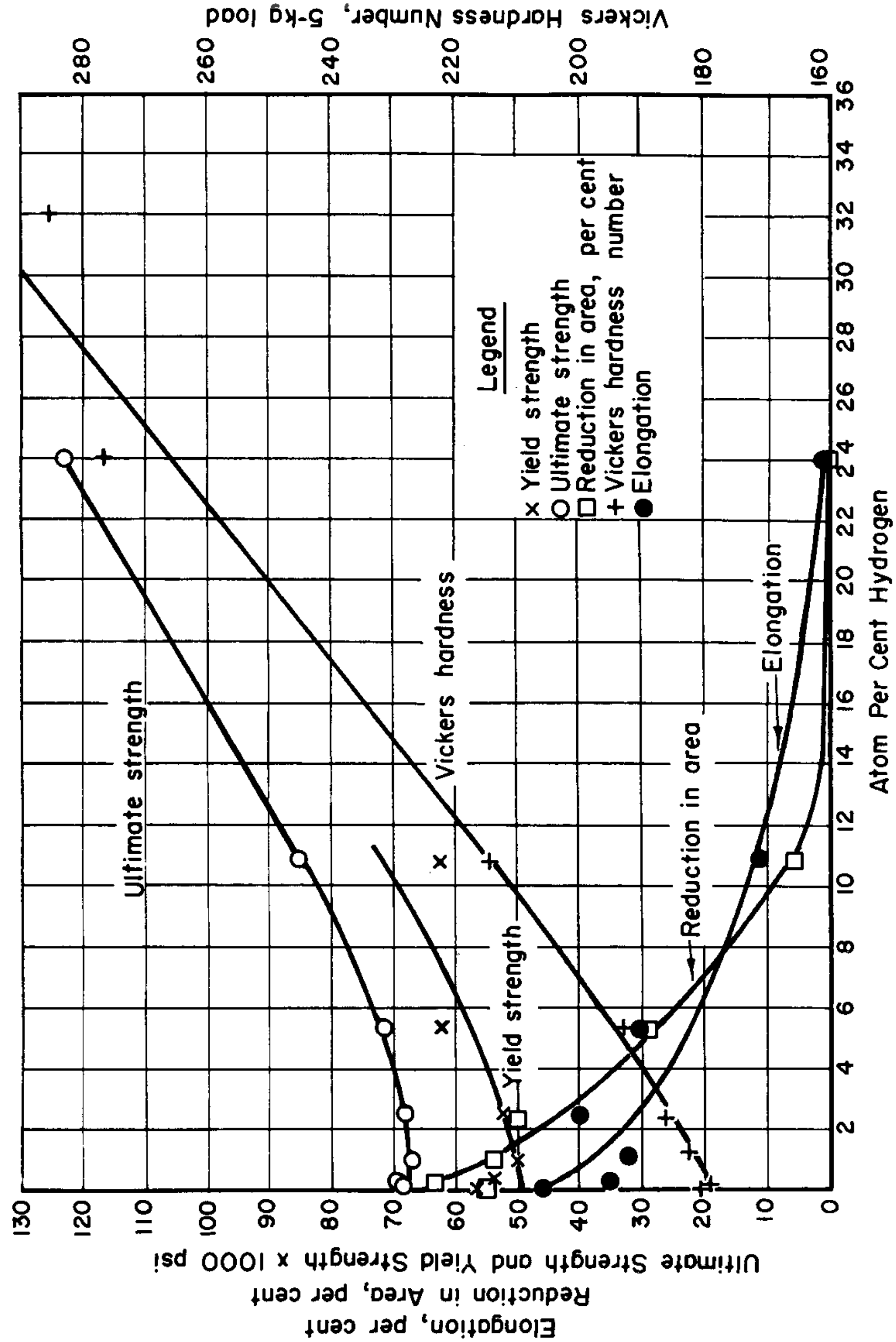

FIGURE 9. VICKERS HARDNESS AND TENSILE PROPERTIES OF COMMERCIAL-PURITY TITANIUM-HYDROGEN ALLOYS

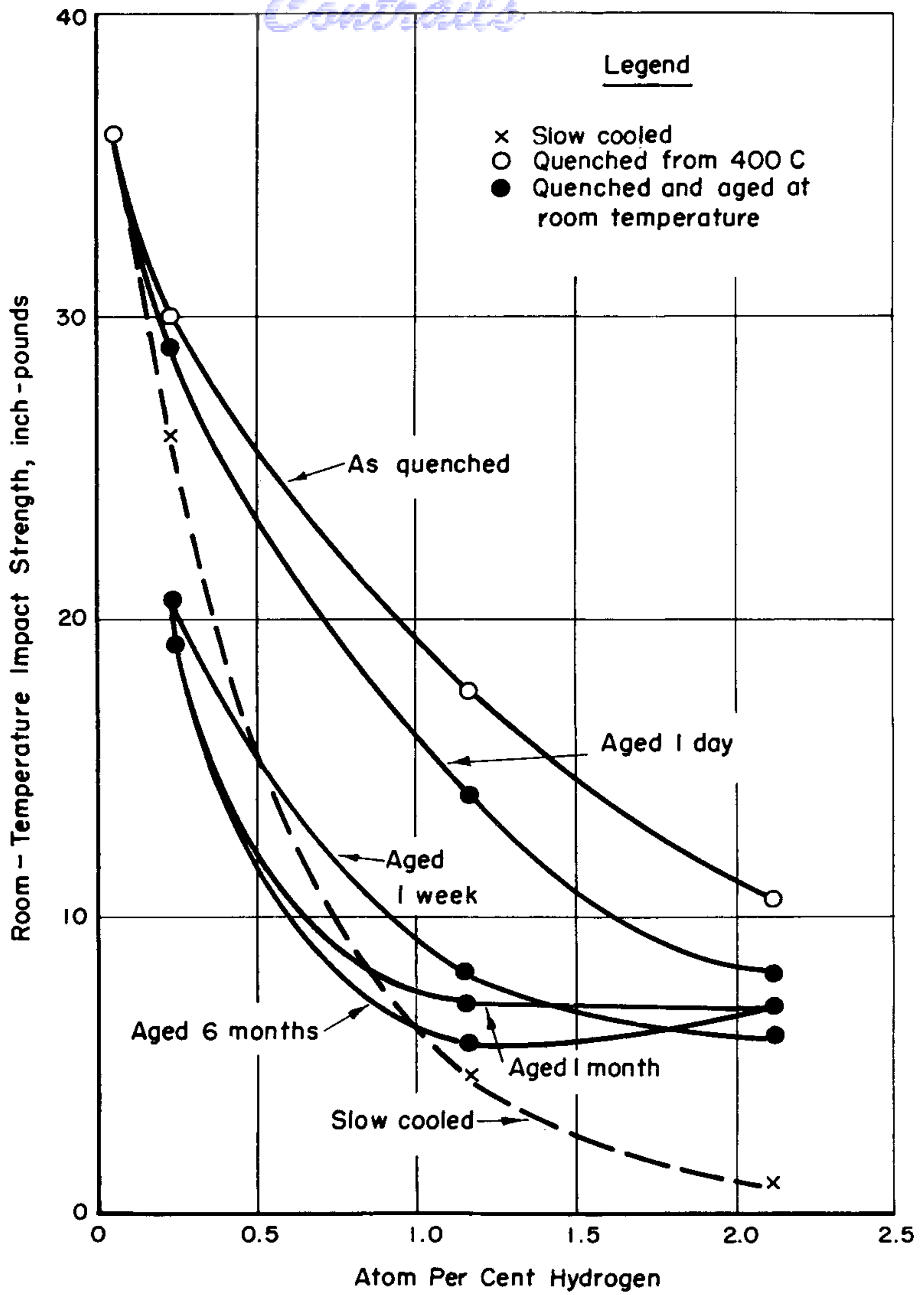

FIGURE 10. EFFECT OF SOLUTION TREATMENT AND ROOM-TEMPERATURE AGING OF COMMERCIALLY PURE RC-55 TITANIUM-HYDROGEN ALLOYS

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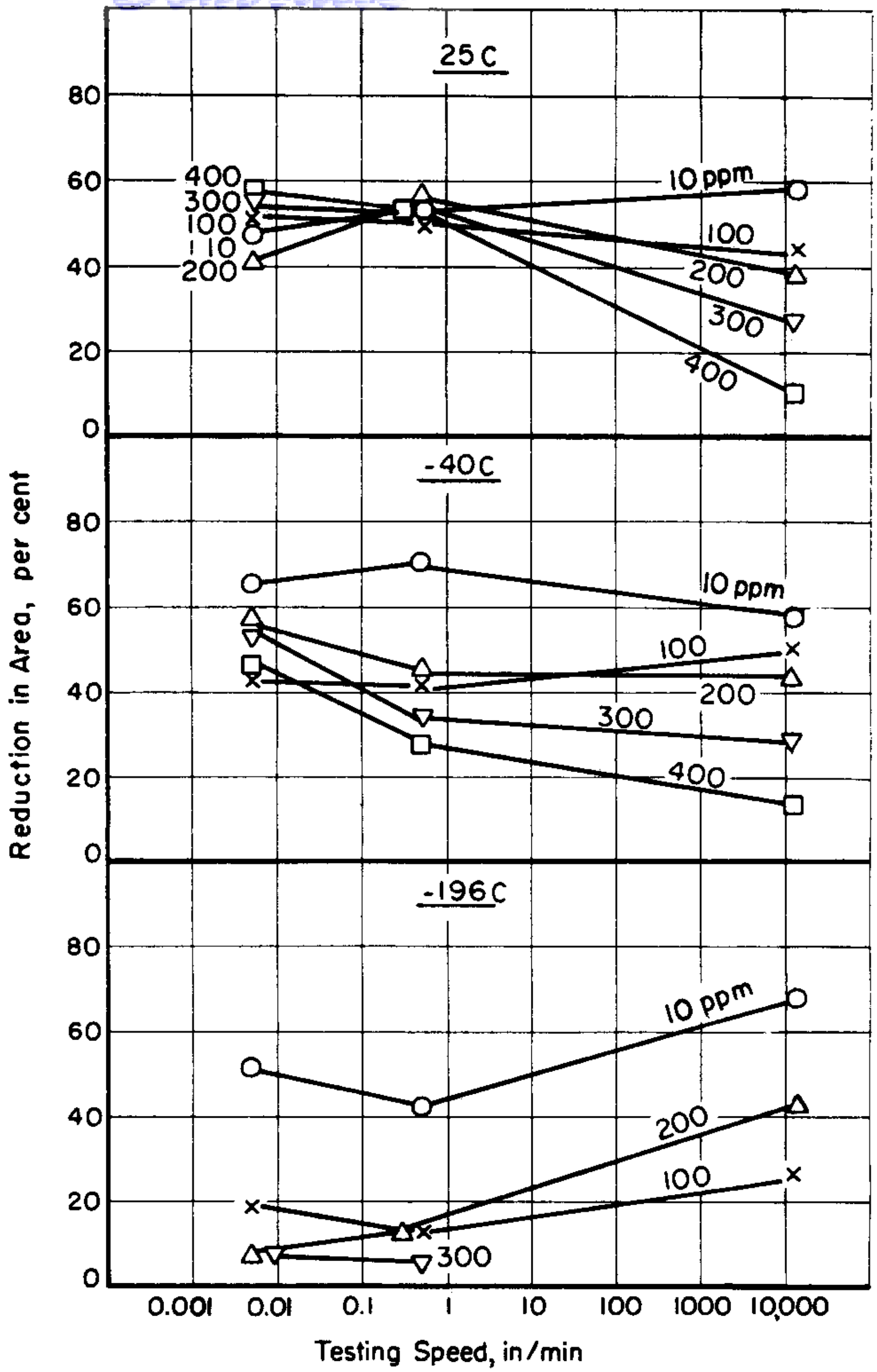

FIGURE 11. STRAIN RATE DEPENDENCE OF UNNOTCHED TENSILE PROPERTIES OF COMMERCIAL TITANIUM AT VARIOUS HYDROGEN LEVELS

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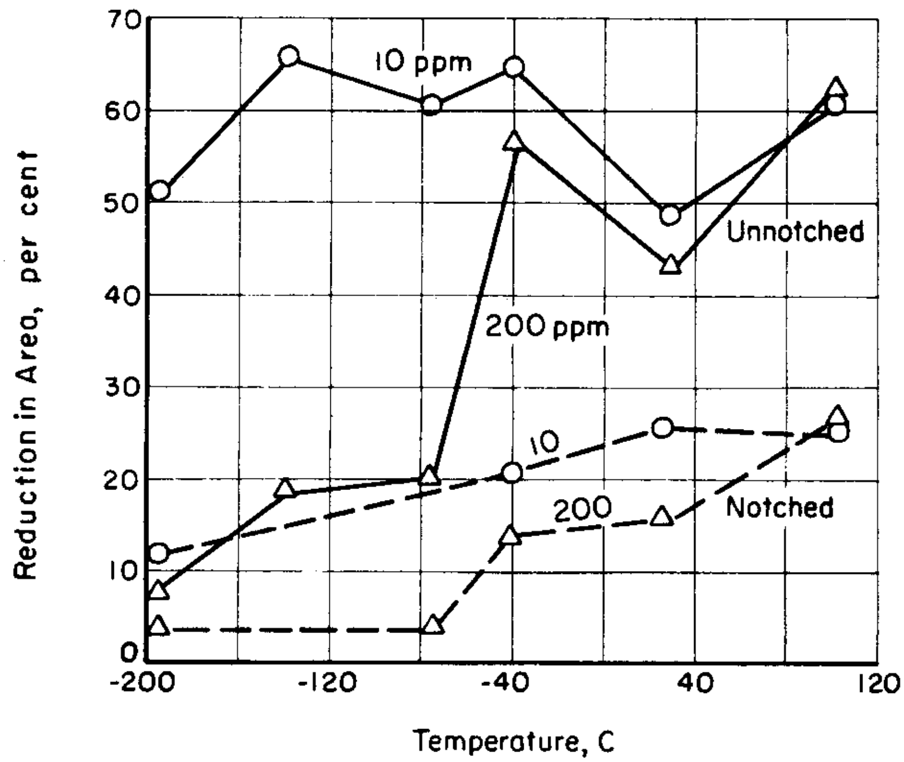

FIGURE 12. TENSILE TESTS ON NOTCHED AND UNNOTCHED COMMERCIAL TITANIUM WITH AND WITHOUT HYDROGEN

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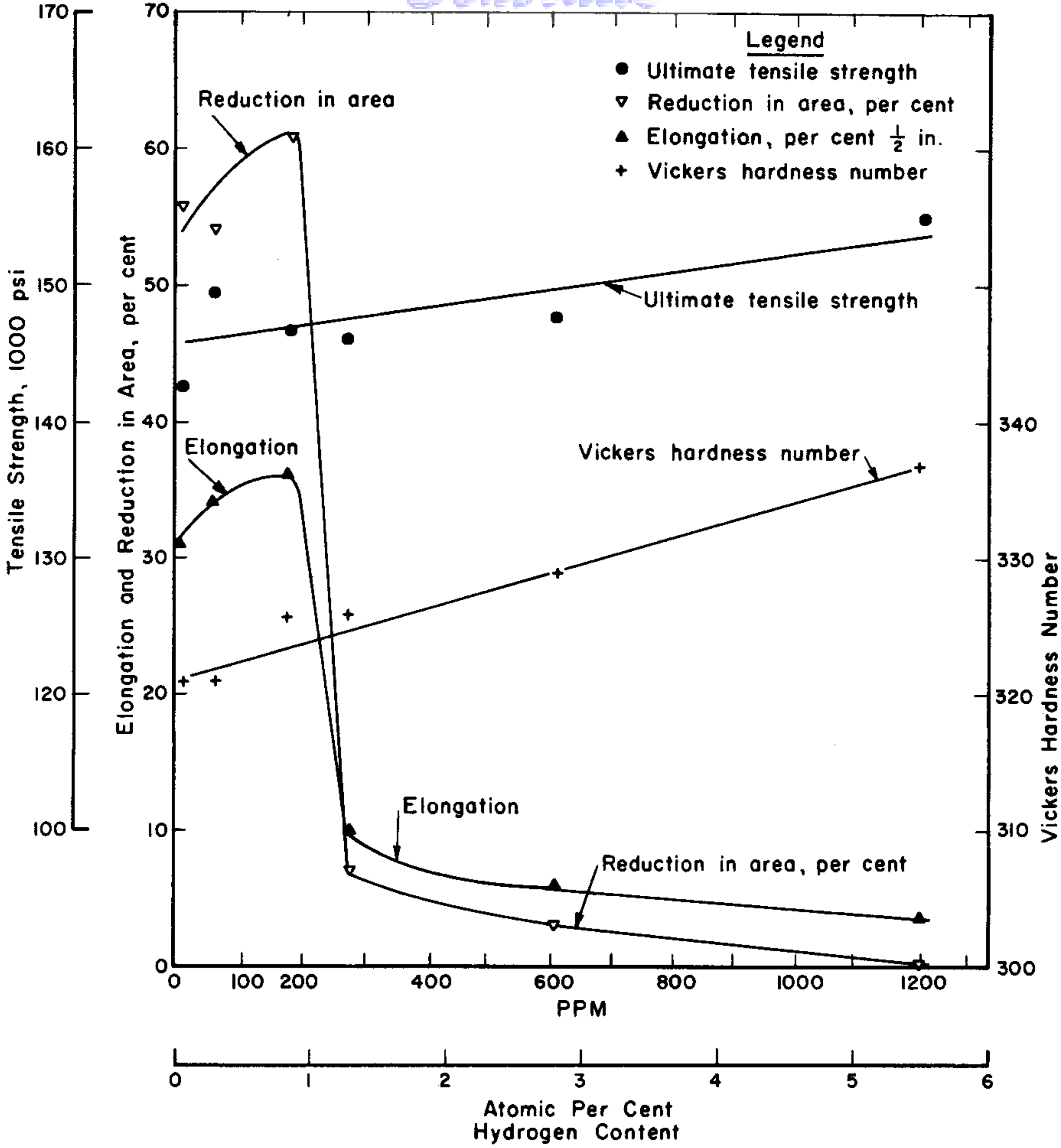

FIGURE 13. EFFECT OF HYDROGEN ON THE TENSILE AND HARDNESS PROPERTIES OF RC 130 A (8 Mn) ALLOY

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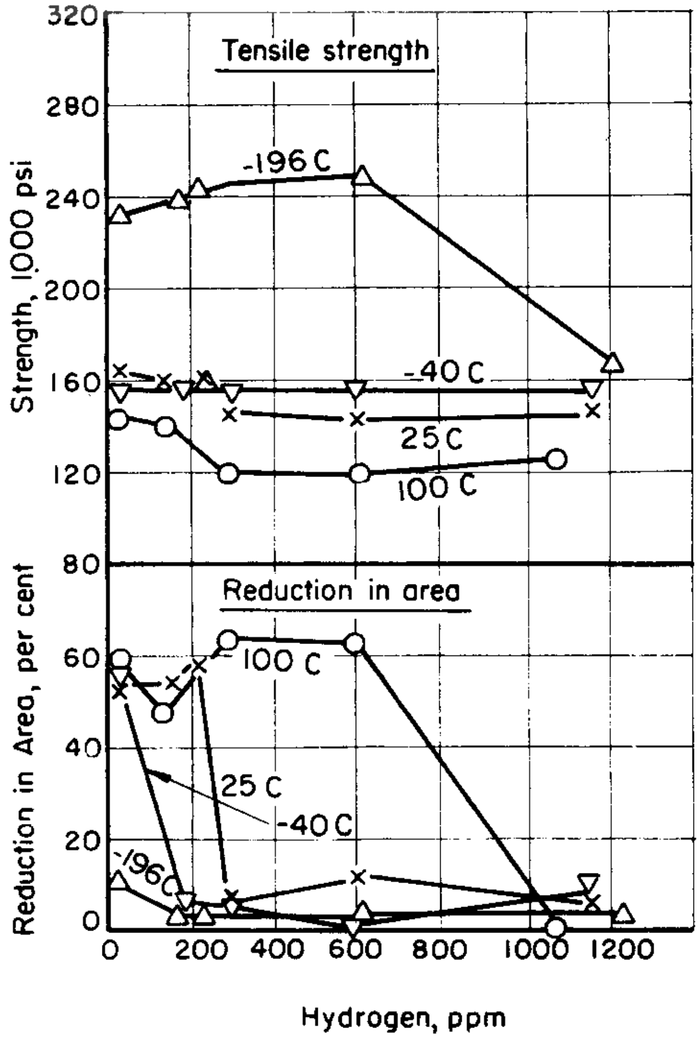

FIGURE 14. TEMPERATURE DEPENDENCE OF SLOW UNNOTCHED TENSILE PROPERTIES OF 8 PER CENT Mn ALLOY CONTAINING HYDROGEN

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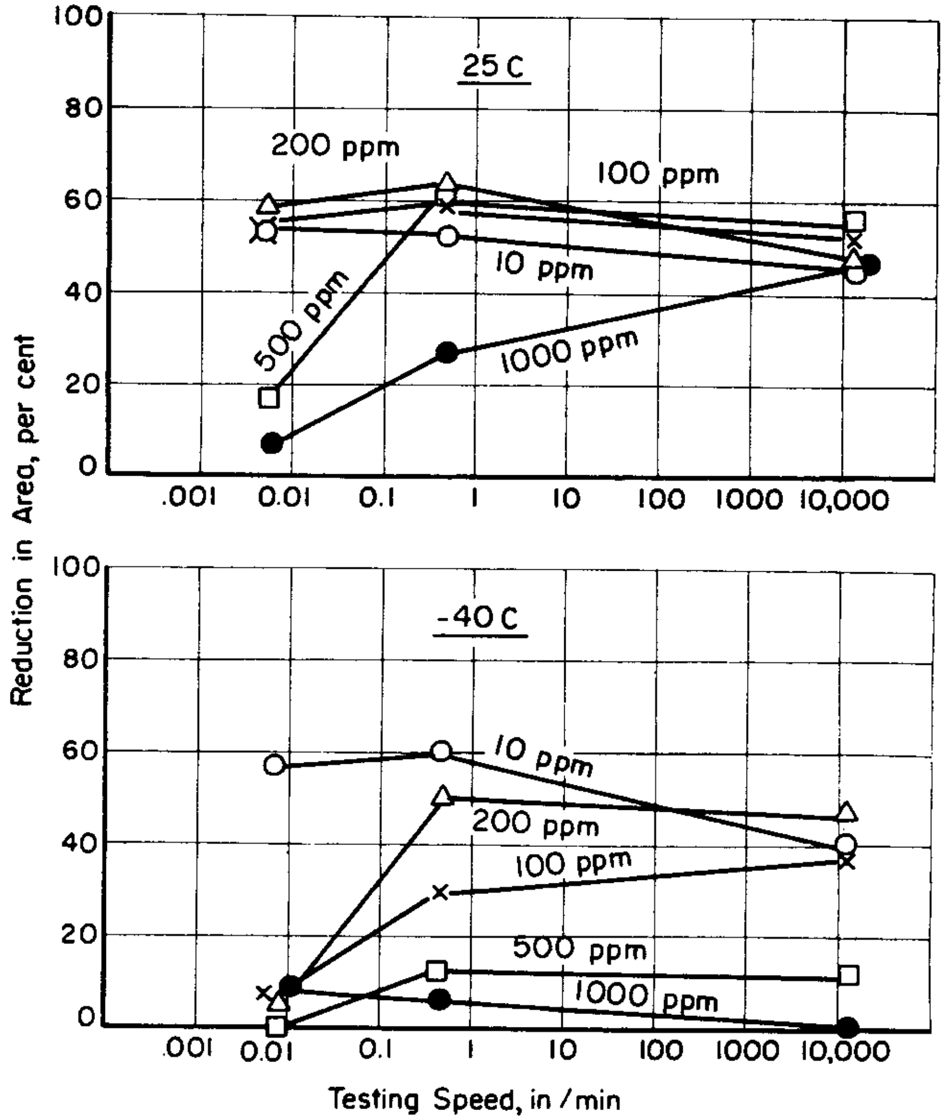

FIGURE 15. STRAIN RATE DEPENDENCE OF UNNOTCHED TENSILE PROPERTIES OF 8 PER CENT Mn ALLOY CONTAINING HYDROGEN

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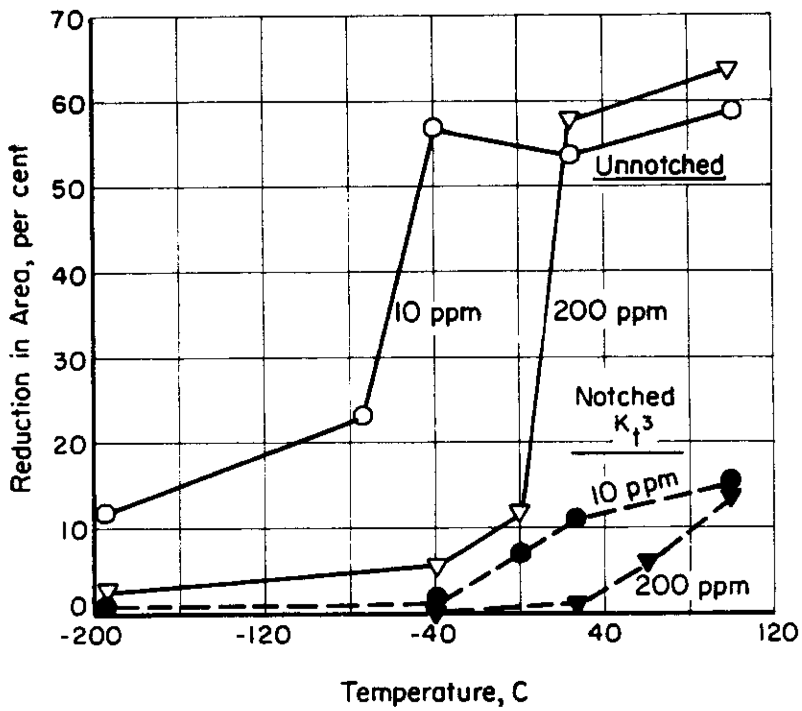

FIGURE 16. NOTCHED AND UNNOTCHED TENSILE DUCTILITY OF 8 PER CENT Mn ALLOY WITH AND WITHOUT HYDROGEN AT VARIOUS TEMPERATURES

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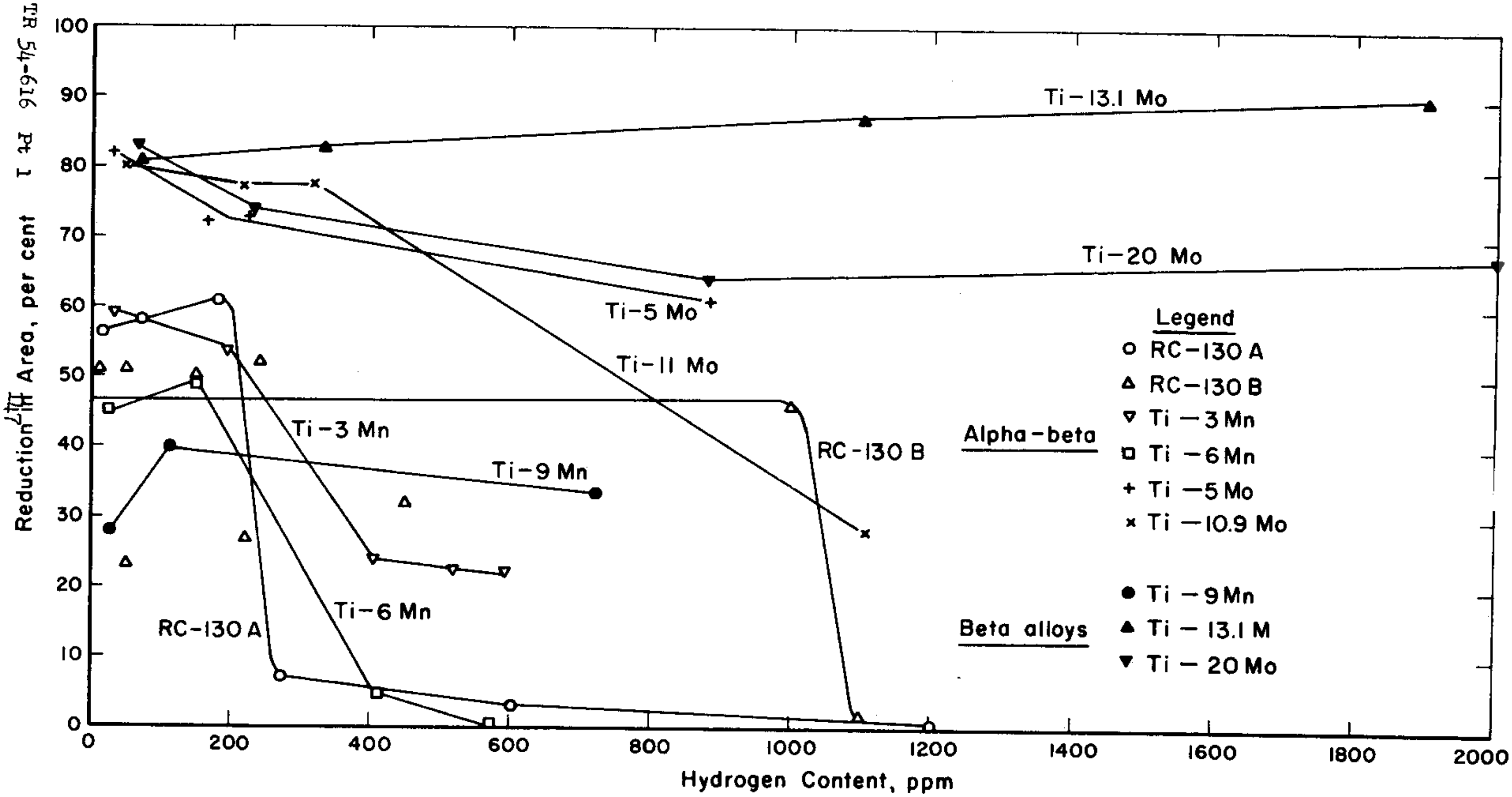

FIGURE 17. EFFECT OF HYDROGEN ON THE REDUCTION IN AREA OF SEVERAL ALPHA-BETA AND BETA TITANIUM ALLOYS

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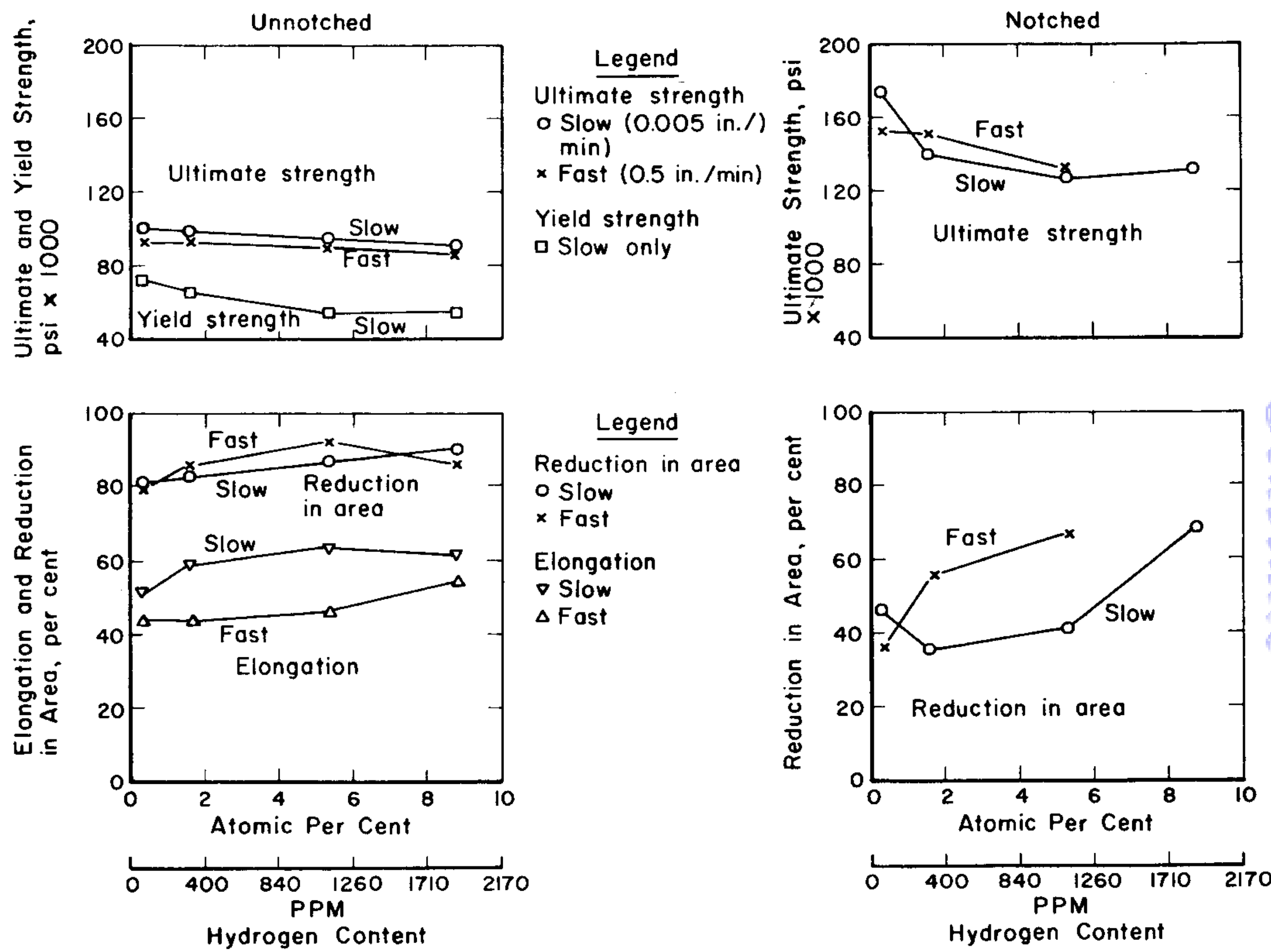

FIGURE 18. UNNOTCHED AND NOTCHED TENSILE DATA FOR TITANIUM—13.1 PER CENT MOLYBDENUM ALLOY AT 4 HYDROGEN LEVELS

0-22462

HYDROGEN LEVELS IN TITANIUM ALLOY

MATERIALS USED FOR CURRENT AIRCRAFT AND ENGINE PRODUCTION

by

Lt J. W. Seeger

The information presented in previous papers has shown some of the ways in which hydrogen contamination affects the properties of titanium alloys. Several months ago, when this investigation was begun, it was seen that the immediate significance of these results would be measured in terms of the amount of material in the hands of airframe and engine manufacturers that could be expected to be susceptible to this embrittlement.

Any elaborate sampling program designed to determine this quality level would be difficult to coordinate with the twenty to thirty companies actively working with commercial alloys. Therefore, the simplest plan was followed. Headquarters, Air Material Command, through its Quality Control field representatives, contacted a major portion of airframe and engine contractors, requesting samples of material currently in use for production or advanced development projects. The response to this request, and to a similar request to forgings producers, was exceptional.

The materials received are being evaluated in two ways: first, by hydrogen and oxygen analyses; and second, by tensile and stress rupture testing. Several of the preceding papers have presented data obtained on materials received from the field, and the work is continuing.

The following illustrations show the analyses obtained on these materials. First, for 8 Mn alloy sheet (Figure 1) a sample of 52 heats yields a distribution of hydrogen analyses as shown, with 50% of the heats above 150 ppm. Hydrogen analyses of six commercially pure heats, not shown here, range from 150 ppm to 200 ppm.

Oxygen analyses have not been obtained on all of these heats, but a sample of 18 heats has the distribution shown in Figure 2. Analysis of 5 heats of commercially pure shows oxygen levels of about the same values.

An interesting view of this data is obtained by plotting hydrogen level against sheet thickness, as shown in Figure 3. Here the variation in hydrogen content from heat to heat that a purchaser might expect to receive becomes greater as the sheet thickness decreases.

Perhaps this indicates that mill processing itself is responsible: the sheet picks up additional hydrogen with added rolling passes and descaling operations. That the hydrogen levels can be constant for various thicknesses of sheet may mean, however, that the descaling operation is responsible rather than the rolling.

Rem-Cru has published a curve (Figure 4) showing what can happen with a hydrofluoric-nitric acid pickling bath of varying nitric concentrations. Hydrogen can be introduced in great amounts if the pickle composition is not controlled. Conversely, hydrogen pickup from this source can be avoided with a properly controlled pickle.

Figure 5 shows the hydrogen levels of forging alloys received from the field. The vertical reference line indicates the 125 ppm hydrogen level which from previous papers has been pointed out as a maximum permissable level to avoid embrittlement of forging alloys.

Additional hydrogen analyses of these alloys were submitted by a forgings producer, and are shown in Figure 6.

All of the hydrogen analyses presented thus far have been obtained by the vacuum fusion method. Battelle Memorial Institute was the source for hydrogen analyses at the beginning of this investigation, with other sources accepted if Battelle results could be duplicated. The ignition method used by Frankford Arsenal was checked early in the program against samples previously analyzed by Battelle, and Figure 7 shows a comparison of results by the two methods.

A Battelle value, if duplicated, would fall on the middle 45 degree line. To either side are lines representing a deviation of 20%. The ignition method failed to reliably duplicate vacuum fusion analyses.

Vacuum fusion equipment newly installed in the WADC Materials Laboratory was checked against Battelle analyses, and the results are shown in Figure 8. The samples analyzed by the two laboratories were most often taken from random locations in the bar or sheet, not adjacent to one another, so the correlation of analyses by the two laboratories using the same method is quite acceptable.

The fact that a number of analytical methods have been proposed for hydrogen determinations, and that variances undoubtedly exist even between laboratories using the same method leads to some difficulties in writing a workable chemistry specification.

Therefore, steps are being taken to determine the extent of disagreement that may exist between two laboratories analyzing random samples of a heat, possibly by different analytical methods. Materials are being supplied by each producer representing nearly all alloy and commercially pure grades of titanium, and these will be distributed to a number of participating laboratories. The program consists of two parts:

Part One - Interlaboratory Variance. Identical samples will be analyzed by all known analytical methods.

Part Two - Sampling Variance. Random samples of a single heat will be analyzed by a single laboratory.

The following laboratories have indicated a desire to participate in this round robin on hydrogen analysis:

Watertown Arsenal
Frankford Arsenal
Naval Research Laboratory
WADC Materials Laboratory
The Ladish Company
Wyman-Gordon Company
Steel Improvement & Forge Company
Pratt & Whitney Aircraft
Brush Development Laboratory
General Electric Company - Evendale Laboratory
General Electric Company - Thomson Laboratory
Westinghouse Electric Corporation
E. I. DuPont de Nemours & Company
Dow Chemical Company
Electro Metallurgical Company
Chase Brass & Copper Company
National Research Corporation
Battelle Memorial Institute
Mallory Sharon Titanium Corporation
Rem-Cru Titanium, Incorporated
Republic Steel Corporation
Titanium Metals Corporation - Henderson Laboratory
Allegheny Ludlum Steel Corporation - Brackenridge Laboratory

A preliminary round robin has already been undertaken between the four titanium producers, Battelle Memorial Institute, and the WADC Materials Laboratory, to determine the steps necessary to obtain identical samples for distribution under Part One of the program - Interlaboratory Variance. There is some disagreement among the producers in the analyses received thus far, as was expected by all. Happily, it is in the few instances one that affords the customer a margin of safety.

Comments on the analytical methods to be used by the twenty-three laboratories participating in the round robin on hydrogen analysis are presented in the next paper.

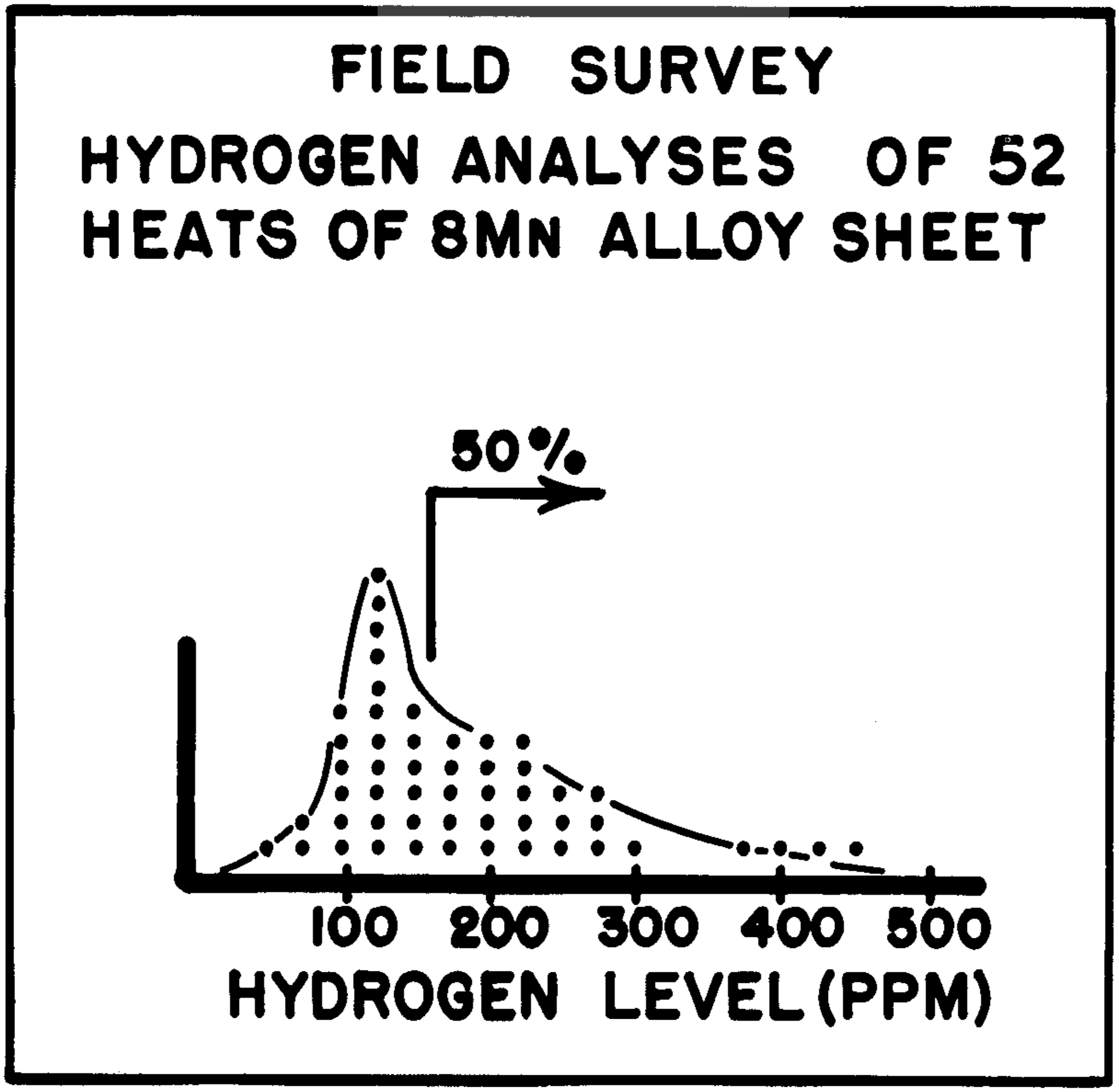

Figure 1

Frequency Distribution of Hydrogen Analyses of 8 Manganese Alloy Sheet Submitted by Airframe and Engine Manufacturers.

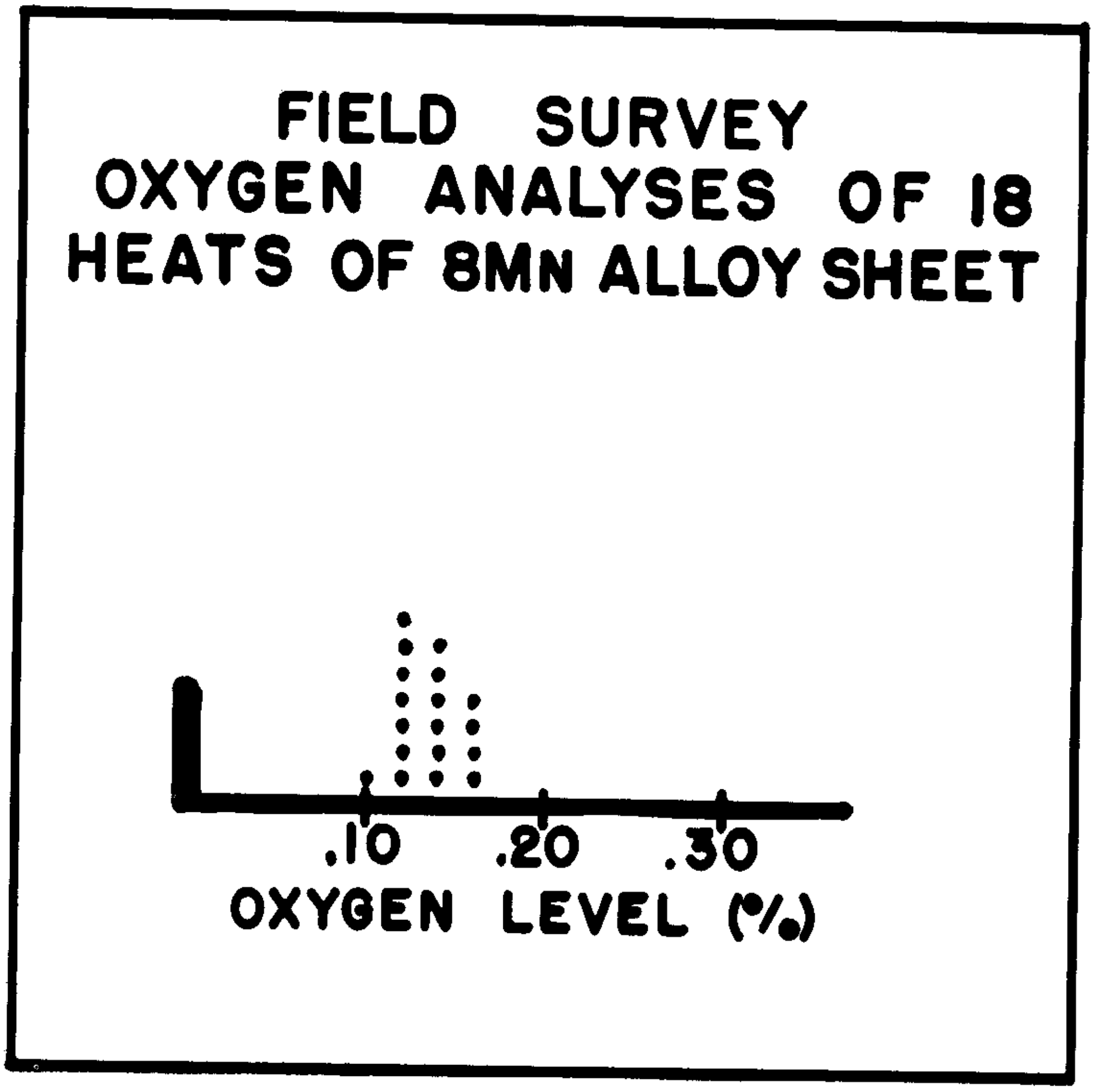

Figure 2

Frequency Distribution of Oxygen Analyses of 8 Manganese Alloy Sheet Submitted by Airframe and Engine Manufacturers.

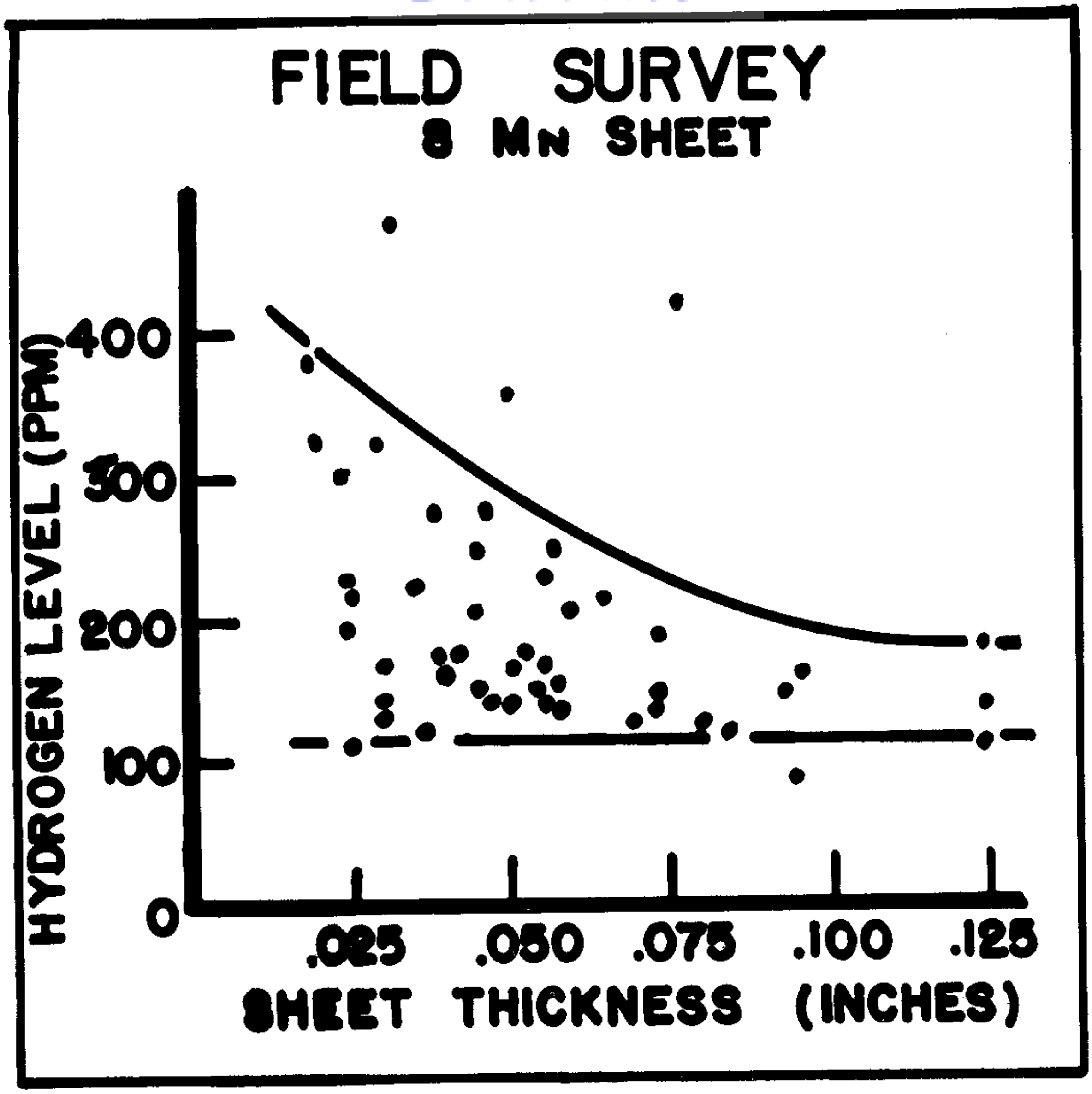

Figure 3

Hydrogen Analyses of 8 Manganese Alloy Sheet at Various Sheet Thicknesses. Material Submitted by Airframe and Engine Manufacturers.

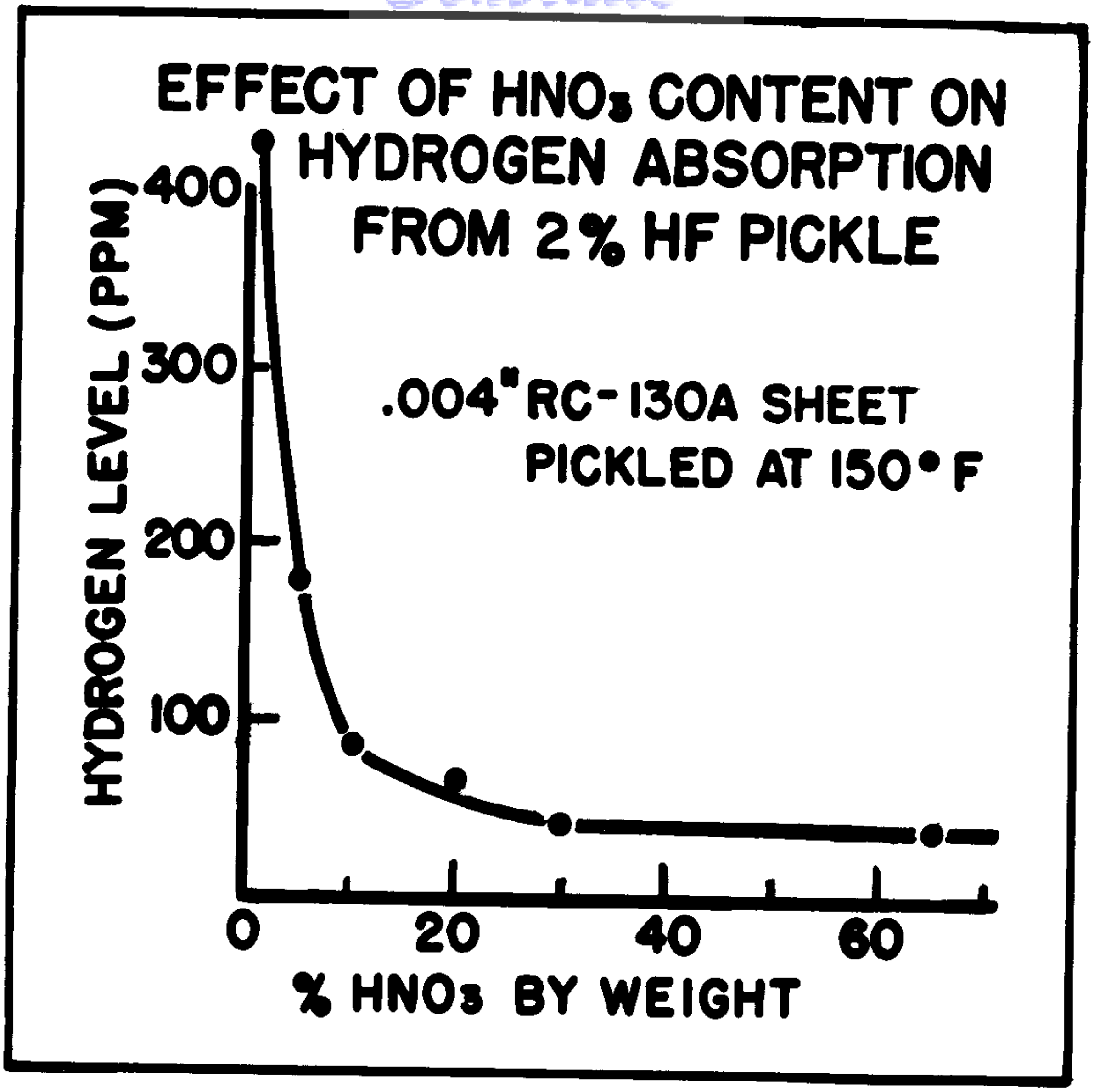

Figure 4

Hydrogen Absorption from Hydrofluoric-Nitric Acid Pickle with Varying Nitric Acid Composition.

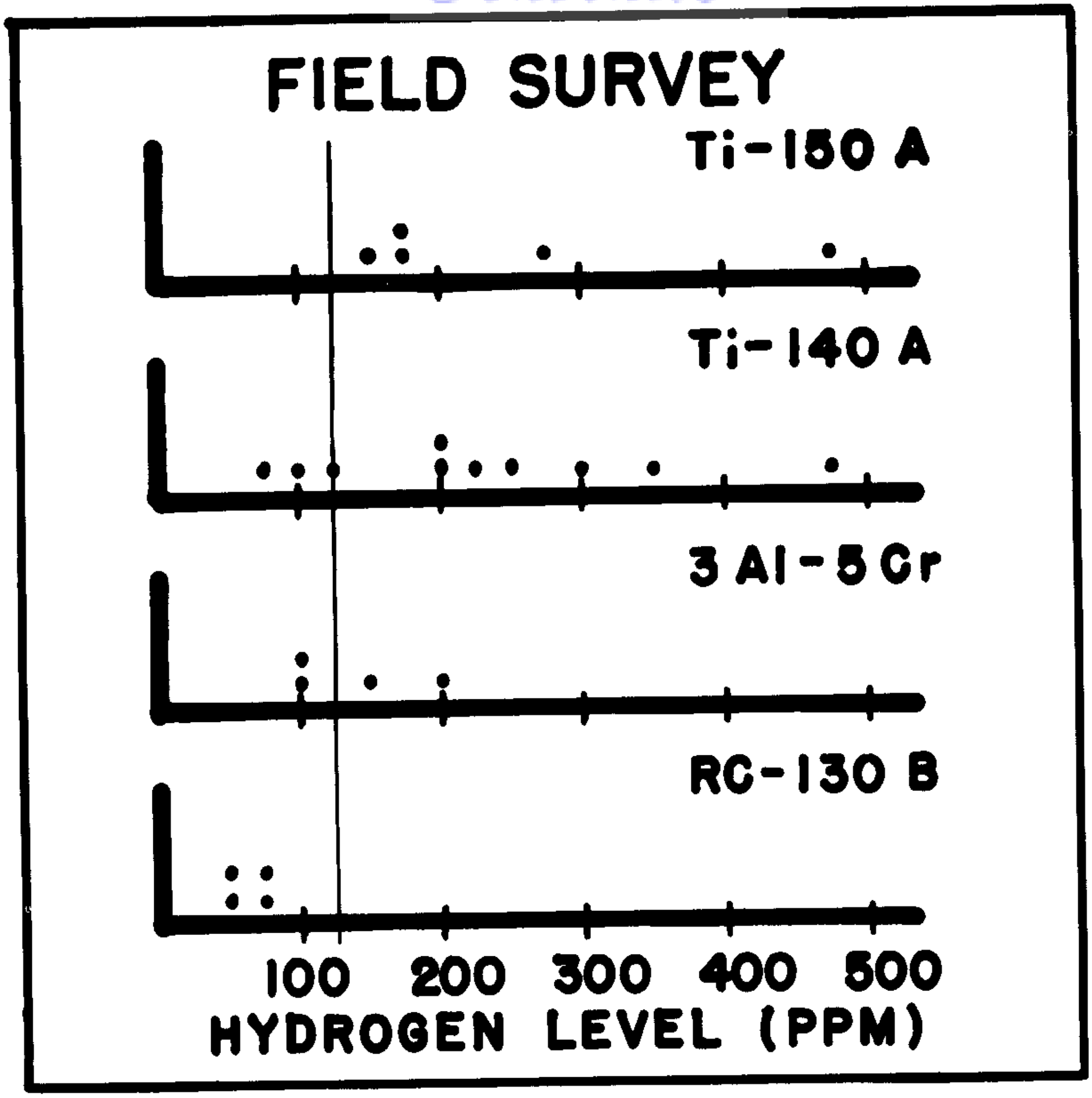

Figure 5

Frequency Distribution of Hydrogen Analyses of Various Alloys Submitted by Airframe and Engine Manufacturers and Forgings Producers.

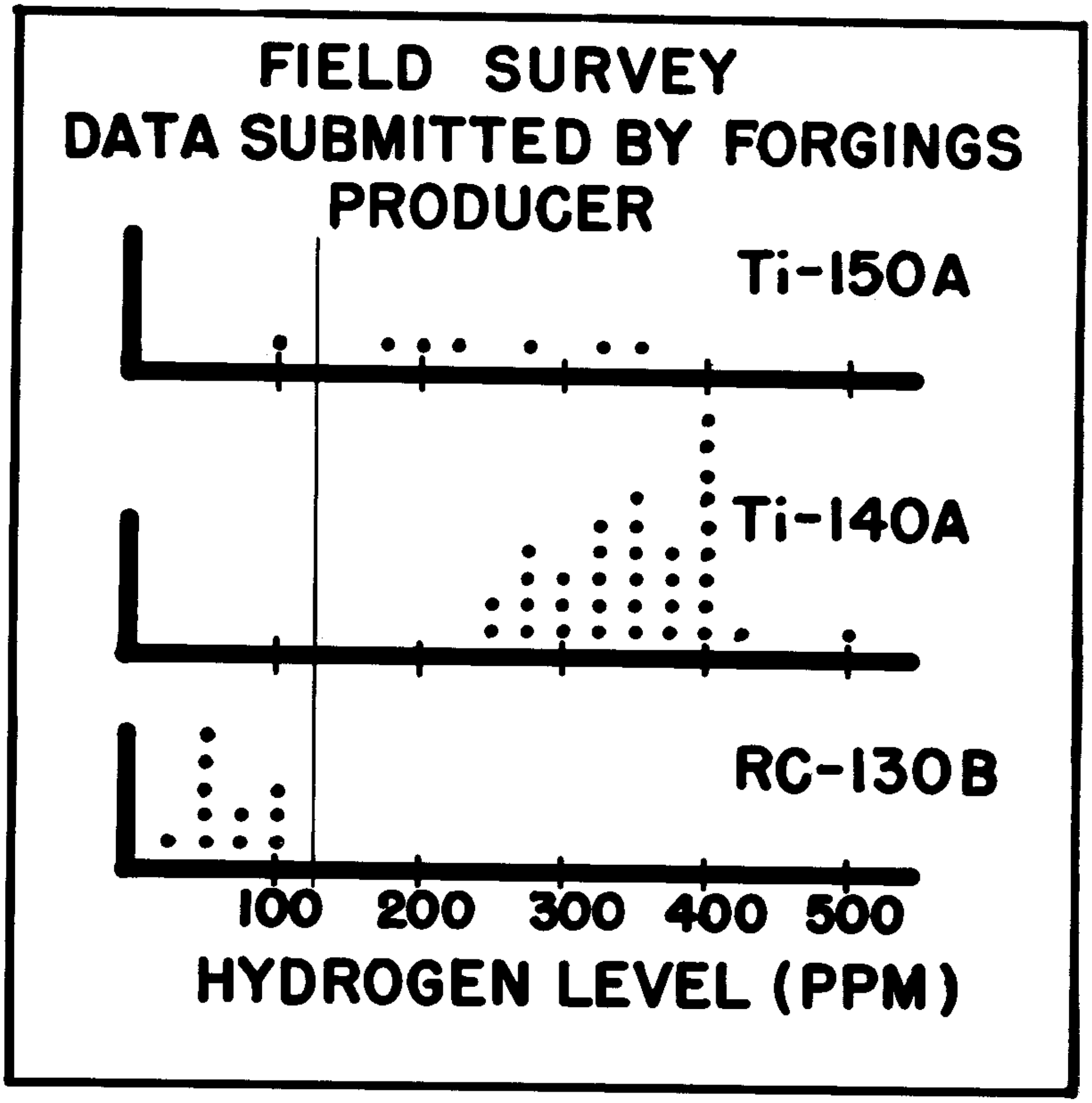

Figure 6

Frequency Distribution of Hydrogen Analyses of Various Alloys. Data Submitted by a Forgings Producer.

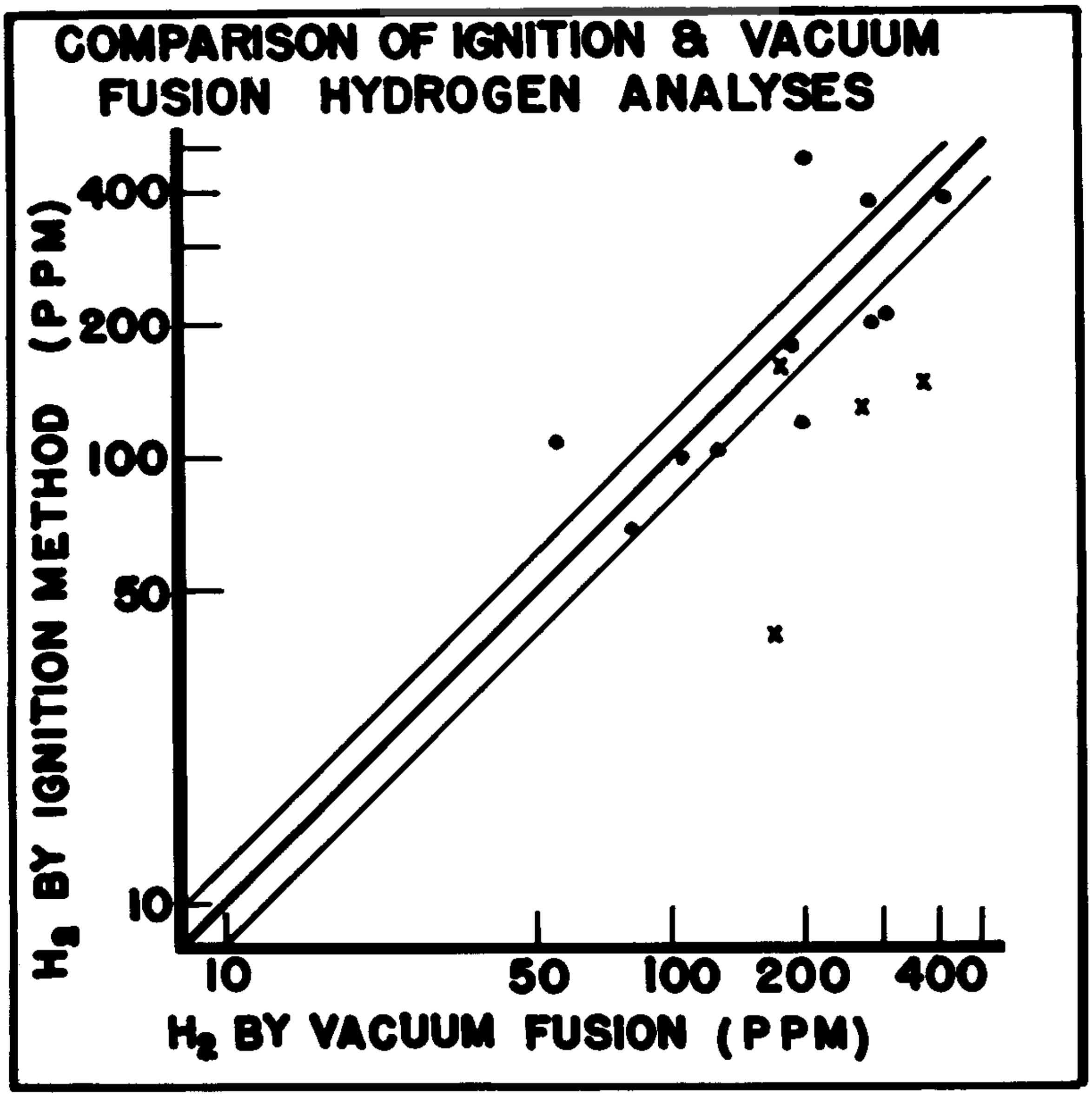

Figure 7

Comparison of Ignition and Vacuum Fusion Hydrogen Analyses.

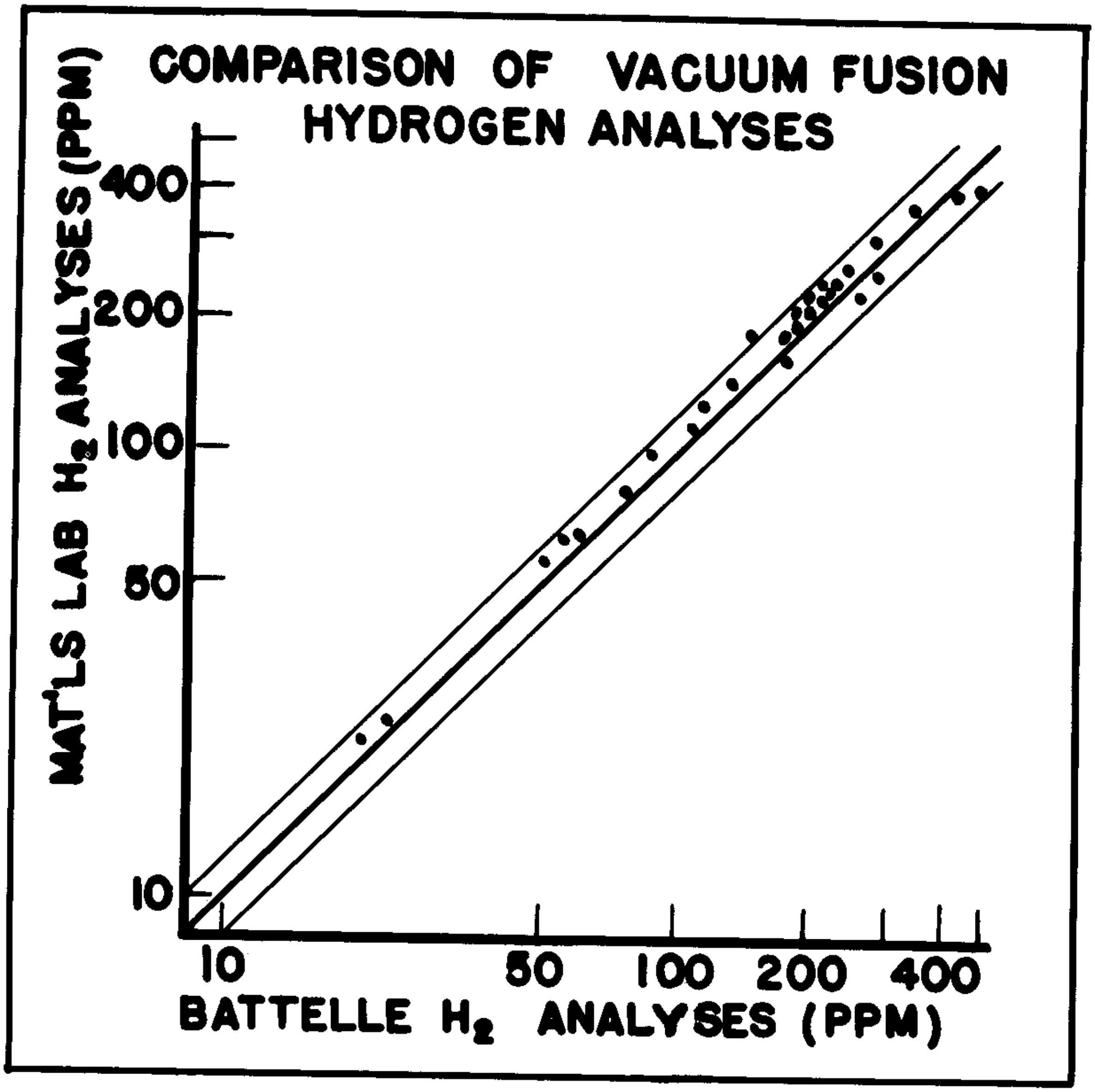

Figure 8

Comparison of Vacuum Fusion Hydrogen Analyses by Two Laboratories.

ANALYSIS OF TITANIUM

by

R. E. Brocklehurst

The analysis of titanium is not quite as difficult now as it was a few years ago; however, there are still problem areas. As methods soon to be published by the Panel on Methods of Analysis, National Advisory Committee on Titanium, will show the chemists have satisfactory methods for the analysis of all metallic alloying elements and impurities with the possible exception of tungsten, magnesium, and aluminum in impurity levels.

Spectrographic analysis of titanium shows promise of becoming a useful tool as it is in the steel or aluminum industries. At the present time this is only a promise, since the only methods which have been published require the metal to be dissolved and the analysis made on the solution. Most spectrographers consider this a slow and bothersome procedure. The results of a current Air Force contract showed that most commercial alloys are sufficiently homogeneous to allow spectrographic analysis to be made directly on the metal samples. The Materials Laboratory, Directorate of Research, Wright Air Development Center plans to go ahead to the next phase and have metal standards made for the commercially available alloys.

Having disposed of a large part of the analysis of titanium with what is probably a great deal of over-simplification, the interstitial elements must be discussed.

Here, again, part of the elements can be disposed of in a hurry. The conventional chemical methods - particularly the steam distillation micro-kjeldahl method - are very satisfactory for the analysis of nitrogen in titanium. This analysis requires about fifteen minutes per sample after the metal is dissolved.

The analysis of carbon in titanium does not seem to pose any special problem, either. Combustion methods - particularly using tube furnaces apparently work very satisfactorily. Several laboratories have reported difficulty in using the newer high-frequency furnaces; however, recent reports from our laboratory and other laboratories indicate that the high-frequency methods of inducing combustion can be used satisfactorily.

Now we come to our enemy and constant companion - hydrogen. There are various ways to classify the methods for determining hydrogen in titanium; however, in general there are three principle methods now in use.

The first method to be presented is the one which has probably been discussed most. This is vacuum fusion method. Actually there are two different ways of using the equipment used for vacuum fusion analysis. One of the ways is by producing fusion of the sample by temperatures of about 1900°C and by collecting and measuring by a method of differences the amount of water formed after oxidation of the hydrogen. This method is very time comsuming, since only ten to twenty complete vacuum fusion analyses can be completed in a forty hour week. In spite of this disadvantage this method is the only method which has been tried out on a large scale and probably must be considered the referee method.

The other way of using vacuum fusion equipment might also be classed with the next method to be presented which is vacuum extraction. In this case a temperature of about 1400°C is used to drive out the hydrogen which is collected and measured as a pressure in a known volume without conversion to water. This method is much faster than the complete vacuum fusion analysis, requiring about one-half hour per analysis. This is about as fast as any method being used. There seems to be some question among the people using this method that all the hydrogen, but only hydrogen, is driven out at these temperatures. Some people have reported that high blanks have been obtained after alloys were analyzed. This indicates that gases are still coming off after the normal analytical period is completed.

The vacuum extraction method is similar to vacuum fusion analysis in that the hydrogen is extracted from the metal and measured as a pressure in a known volume. Aside from some minor differences in the size of the samples used and the way the gas pressure is measured the major difference is that in the vacuum extraction method uses a quartz furnace tube heated externally by a Glo-bar furnace. This limits the extraction temperature to about 1050°C. There may be some question that all the hydrogen is extracted at this temperature. The major advantage in the vacuum extraction technique is that the equipment is much less expensive.

The equilibrium pressure method depends on the fact that in single phase titanium under equilibrium conditions dissolved hydrogen behaves as an ideal liquid and conforms to the Clausius-Clapeyron equation. Stated simply this means that a linear relationship exists between the logarithm of the equilibrium pressure of the gaseous hydrogen and the logarithm of the concentration of hydrogen in the metal under isothermal conditions. The temperature normally used is 1000°C. This is accomplished in individual quartz sample tubes with a nichrome heating mantle. With this method complete removal of hydrogen does not occur and is not necessary. The hydrogen content is determined by adding the quantity shown to be still in the metal by the equilibrium pressure to that measured in the gaseous state. One disadvantage of this method is that a somewhat different relationship exists for each alloy type, so the type must be determined if it is not known and several pressure concentration curves used. The principal advantage is that this equipment, too, is much less costly than vacuum fusion equipment.

The last technique which has been used to determine the hydrogen content is the combustion technique. There have been two modifications of this method reported. One is the macro technique and the other the micro technique. The macro method uses conventional combustion tubes and furnaces and the micro method uses a train similar to that used for the micro-chemical determination of carbon and hydrogen in organic materials. The principal difference in the two methods is the quantity of sample used, the macro method requiring ten grams and the micro method one-half gram. Both methods depend on complete oxidation of the sample and determination of the hydrogen by collecting and weighing the water produced. The results obtained by the macro method as determined by a contractor have shown very poor agreement with the results obtained by vacuum fusion. The principle advantage of these methods is that the equipment is probably the cheapest of all.

A few methods such as nuclear magnetic resonance and neutron scattering have been proposed, but they have not been investigated. Figure 1 shows a comparison of time required and initial cost for each method of hydrogen analysis.

The most difficult of all the elements which must be determined in titanium is oxygen. Vacuum fusion analysis has been the only method of determining oxygen which has been used successful by many laboratories. This means the long, laborious technique discussed earlier. There are no short cuts. All this work has been reported by the Panel on Methods of Analysis.

A few alternate methods of analysis have been proposed. Three of these involve decomposition of titanium by halogens. At least one laboratory has used a chlorination technique which converts the titanium to volatile titanium tetrachloride with the exception of that which is converted by the oxygen to titanium dioxide. This non-volatile residue is analyzed for titanium colorimetrically and the oxygen calculated from this result. Unfortunately most of the results obtained by this method are low in comparison with those obtained by vacuum fusion. There are good reasons for this. The reasons are that any carbon in the metal reacts to form carbon monoxide with a consequent loss of oxygen; if the temperature is not carefully controlled chlorine can partially reduce the titanium dioxide and some alloying elements take part of the oxygen in forming oxychlorides. Probably corrections could be made for some of these factors.

A second method using a bromination technique in the presence of an excess of carbon overcomes the previous difficulty. This method, developed by Codell at the Frankford Arsenal, introduces bromine to a reaction tube by bubbling helium through bromine. In this reaction all the metal is converted to volatile materials. The titanium to titanium tetrabromide and the oxygen to carbon monoxide which is converted to carbon dioxide by a tube of cupric oxide. The carbon dioxide is collected and weighed in the usual manner. This method looked good the few times it has been compared with vacuum fusion results but it will require further checking.

A third method developed by Dr. Hoekstra of the Argonne National Laboratory, using hydrogen fluoride, has been suggested; however, it probably would have no advantages over the bromination method.

An entirely different method of analysis will be investigated under a contract originated by this laboratory. This method is based on an experimental observation made by Dr. Dean of the Chicago Development Corp that the anodic electrode potential of titanium in an electrolyte of a fused salt depends on the concentration of oxygen in the anode. Actually, what is determined might more aptly be called an activation constant. If this constant can be related specifically to oxygen without any uncorrectable contribution by alloying elements or other interstitial elements this should prove to be a very worthwhile development, since it would be much faster than any other method. Figure 2 shows a comparison of time required and initial cost for each method of oxygen analysis.

In conclusion, the analysis of hydrogen in titanium is not an extremely difficult or unsolvable problem. The analysis of oxygen will continue to be a more difficult problem.

DISCUSSION

Mallett: I hope that the figures quoted are due to unfamiliarity with the true facts. In our laboratory we can perform four vacuum fusion analyses for oxygen in eight hours. About four hours are required for the first sample with the others coming at the rate of one per hour. Your estimation of a fourteen hour set-up time is completely unrealistic. Thirty minutes should be sufficient.

In regard to the second method of using vacuum fusion for hydrogen the set-up time should be about the same. The running time should be as short as any other method with about ten samples per day completed. The cost of the equipment required for this method can be much cheaper since the complete analysis does not have to be made. In most cases if you just measure the volume of the gas you will find that it is about 95% hydrogen. You could use a pressure measurement or a thermal conductivity measurement. This would speed up the process.

Brocklehurst: I recognize that you know much more about the vacuum fusion than I, since you have been in the business many years. I realize that I probably was too pessimistic as far as the figures go, and I am sorry I gave this impression since I like this method and as far as I know it is the only method of proven reliability. I am surprised that you can outgas your equipment so rapidly.

I would like to point out that I am talking about commercially available equipment - the only one being made by the National Research Corporation, as far as I know. If their very complete and detailed instructions are followed a considerable time is required - at least an hour and a half per sample after the system is outgassed.

Apparently we run samples even faster than you if hydrogen alone is considered. We can determine thirty a day after outgassing.

Mallett: If chlorinated graphite is used the outgas time can be considerably reduced. If the complete vacuum fusion analysis is made, the outgassing must be carried out to a much higher degree since higher temperatures are used. If hydrogen alone is being determined at temperatures of 1400°C or 1500°C the outgassing can be accomplished in one hour.

Brocklehurst: That is true. The nine hours I listed as set-up time included sample preparation, since the operations proceed so rapidly after the analyses are started that there is no time to prepare more samples.

Mallett: Yes, and if you put an extra bulb in your system you can collect gas from one sample while you are measuring another.

Brocklehurst: That is true although we have not considered that a major advantage since we outgas the system while collecting the next one, anyway.

I have heard of the halogented graphite. I will point out that it is much more expensive, however, this is probably not an important consideration in view of the time required.

Mallett: We can buy the crucibles for about the same cost as it costs to machine them in our shops. They cost about $1.25 or $1.50 per crucible in lots of a thousand.

Brocklehurst: As I say I do not want people to take the figures in my charts too literally and I certainly do not want to give a bad impression of vacuum fusion. As I say we use it. I like it, and it is the only method that has been checked out so far.

Bryson: Has anything been done to follow-up the potentiometric method of Dr. Dean's.

Brocklehurst: We are supporting his work financially.

Fowler: Isn't the fundamental difficulty of the halogenation techniques the almost impossibility of getting oxygen-free halogens. This was true in the case of steel analysis.

Brocklehurst: This may be true. Of course considerable effort is made to purify the halogens.

Anonymous: In the comparison of the vacuum extraction and gas equilibrium methods the only difference is that the vacuum extraction method requires a transfer pump in the system while the other does not. The time should be the same - one half hour in each case -, since both are controlled by the same factor - the rate of diffusion of hydrogen. The cost will be the increased cost of the extra pump.

You suggested the residual gas evolution may be oxygen. This does not seem too likely. In the case of steel, which is in the same crystal form as titanium under the analytical conditions, you find residual evolution of hydrogen. If this is a possibility it should be explored.

Brocklehurst: We hope to investigate this residual evolution. My understanding of the two methods was that complete extraction was not required for the gas equilibrium method while it is required in the vacuum extraction method.

Anonymous: It is true that you are not completely extracting hydrogen, however, since the time to reach equilibrium will be the same in either case, the time per analysis will be the same.

Brocklehurst: My only point is that at the temperature of 1050°C does all the hydrogen come off? I don't know.

HYDROGEN ANALYSIS

	ANALYSIS HRS.	SET-UP HRS.	COST $
VAC. FUSION I	4	14	6000-7000
VAC. FUSION II	1/2	9	6000-7000
VAC. EXTRACT.	1/2	1	2000-2000
EQUIL. PRES.	1/3	1	2000-3000
COMBUSTION	1	1	500-1000

Figure 1

Comparison of Costs for the Different Methods

OXYGEN ANALYSIS

	ANALYSIS HRS	SET-UP HRS	COST $
VAC. FUSION	4	14	6000-7000
HALOGENATION	2	2	500-1000
POTENTIOMETRIC	1/4	1	1000-3000

Figure 2

Comparison of Costs for the Different Methods

QUALITY REQUIREMENTS FOR TITANIUM AND TITANIUM ALLOYS

by

H. J. Middendorp

USAF SPECIFICATION BULLETIN NO. 108

The first subject presented is a discussion of USAF Specification Bulletin No. 108, Quality Requirements for Wrought Titanium and Titanium Alloys. The bulletin was issued 9 August 1954 after a series of meetings between representatives of WADC, AMC, and the titanium producers. The bulletin was issued to state Air Force quality and capability requirements for wrought titanium and titanium alloys in the producers' plants. Sheet material hydrogen tolerance levels were not included in the bulletin because WADC and the titanium producers had concentrated primary effort in accumulating data on hydrogen tolerance levels for bar, rod, and forging stock; sufficient data were not available at that time for sheet materials. Much of the necessary data have now been accumulated by the Materials Laboratory, WADC, as you have heard previously this afternoon. It is therefore anticipated that Bulletin No. 108 will contain hydrogen tolerance limits for sheet materials in the near future.

The 125 ppm (0.0125 weight percent) maximum hydrogen requirement was established on the meager data available; however, it has been proven by subsequent Materials Laboratory tests to be a tolerance acceptance level which will avoid many hydrogen embrittlement failures in titanium.

SPECIFICATIONS

The next subject presented is specifications for titanium and titanium alloys. Military specifications when initially issued did not include hydrogen tolerance limits for the reason that attention was not focused on the effects of hydrogen at that time. As these specifications are revised, hydrogen and other interstitial contamination tolerance limits will be specified therein. The same situation exists for AMS specifications. At the AMS Division meeting in September 1954, a series of specifications for unalloyed and low alloy titanium was discussed. The titanium producers and airframe manufacturers agreed to a requirement of 250 ppm maximum hydrogen; however, this tolerance level was not based on data, but was a compromise agreement.

Current Military and AMS materials specifications for titanium and its alloys are as follows:

Military

MIL-T-9011 (USAF)	Titanium Bars, Forgings, and Forging Stock
MIL-T-9046 (USAF)	Titanium Alloy Sheet, Strip, and Plate
MIL-T-9047 (USAF)	Titanium Alloy Bars, Forgings, and Forging Stock
MIL-T-7993A	Titanium Sheet, Strip, and Plate (Unalloyed)

AMS

AMS 4900	Titanium Sheet and Strip - 55,000 psi Yield
AMS 4901	Titanium Sheet and Strip - 70,000 psi Yield
AMS 4908	Titanium Alloy Sheet - 8Mn, Annealed - 110,000 psi Yield
AMS 4921	Titanium Bars and Forgings, 99Ti, Annealed, 70,000 psi Yield
AMS 4925	Titanium Bars and Forgings - 4Al, 4Mn, Annealed - 130,000 psi Yield

The Military specifications are listed in AF Bulletin No. 23, and the AMS specifications in the AMS Specification Index.

The AMS Division is preparing two additional specifications; one for Titanium Sheet and Strip - Annealed - 40,000 psi Yield and another for Titanium, Low Alloy, Sheet and Strip, 70,000 psi Yield; the latter is a 1% manganese alloy.

Many Air Force contractor materials specifications have been issued; however, WADC prefers that Government or AMS specifications be used. Such policy is stated in ANA Bulletins 143, Use of Specifications and Standards; 147, Specifications and Standards of Non-Government Organizations; and 343, Use of Specifications and Standards Applicable to Aircraft Engines and Propellers.

QUALITY

The next subject is quality requirements. Production of constant aircraft quality titanium and titanium alloys from heat to heat is essential for processing and fabrication into airframe, missile, and engine components for USAF Weapons Systems. The titanium producers have made improvements in such factors as drying of sponge prior to melting, consumable electrode melting, skull melting, melting under partial vacuum, scalping of ingots, and more careful control of pickling and scale removal processes. These and other factors are contributing to the "state of the art" and are necessary in order that titanium and titanium alloys can be used in structural applications for USAF Weapons Systems.

Nondestructive Testing

The next subject is nondestructive testing of titanium and its alloys. A complete dissertation on the subject is not intended, since vast amounts of literature are available from such sources as the equipment producers, technical journals, and various publications of the Society for Nondestructive Testing.

The principal nondestructive test methods used for quality control of titanium are radiography, penetrant inspection, and ultrasonic testing. Conductivity tests have also been used.

Radiography is useful primarily for detecting internal discontinuities. One of the reasons radiography of titanium for use in USAF aircraft was required was that tungsten inclusions were present in much of the early material produced by the tungsten electrode process.

Penetrant inspection has proven a necessary quality control method to detect surface-connected discontinuities such as flash-line cracks, shear cracks, and forging laps. The fluorescent penetrant, contrast dye penetrant, and post emulsification processes are currently used.

Ultrasonic testing of titanium alloy components such as jet engine compressor disks and spacers has proven to be increasingly useful for detection of surface and internal discontinuities. Both the contact scanning and immersed techniques have been used; although the use of the immersed method by Air Force contractors has steadily increased.

One of the most important considerations is establishment of acceptance standards. In general, standards have been based on size of discontinuity as correlated with test blocks having a series of various diameter flat-bottomed drilled holes. Standards must be established by correlation of size, number, nature, distribution, and location of discontinuities with simulated or actual service tests. The latter statement is true for any nondestructive test method.

Sound frequencies in the range of 1/2 megacycle to 25 megacycles are currently in use. Higher frequencies increase ease of resolution for minute discontinuities; however, grain size becomes a limiting factor at the higher frequencies of 15 to 40 megacycles.

Loss of back reflection in testing of compressor disks has been experienced caused by grain size variation or complex configuration of the part. It is essential that such factors be recognized to distinguish between grain size effects and existence of discontinuities.

It is recommended that any Air Force contractor, sub-contractor, or supplier intending to use any of these nondestructive test methods utilize the technical services of the equipment manufacturers, the Materials Laboratory, WADC, and the Air Force Materials and Processes Representatives in Quality Control, AMC, to the fullest advantage.