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Report on

THE EFFECTS OF CARBON, OXYGEN, AND NITROGEN ON
THE MECHANICAL PROPERTIES OF TITANIUM AND
TITANIUM ALLOYS

by

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to

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ABSTRACT

This report reviews the effects of the alpha solute interstitials C, O, and N on the mechanical properties of titanium alloys. These interstitial elements strengthen titanium, although this effect is lost at elevated temperatures. At room temperatures the interstitials have little effect on tensile ductility, but at subzero temperatures they promote embrittlement. They also have a deleterious effect on toughness, notch sensitivity, weld ductility, machinability, and bend ductility.

The strengthening effect of either individual or combined interstitials can be grouped in terms of an oxygen equivalent. It has been found that 0.1 per cent nitrogen is approximately equivalent to 0.2 per cent oxygen or 0.3 per cent carbon. Thus, the oxygen equivalent becomes

$$\text{oxygen equivalent} = \%O + 2 \times \%N + 2/3 \times \%C.$$

The oxygen equivalent is related to hardness as follows:

$$\text{Bhn} = 40 + 310 \sqrt{\text{oxygen equivalent}} .$$

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FOREWORD

This report is based on information obtained from a survey of research reports and published documents. In this report, the effects of the interstitials on many properties are discussed. Other factors affecting these properties are not discussed in this report because they are covered in detail in other TML reports, namely:

TML-8 Principles and Practical Aspects of Titanium Heat Treatment.

TML-15 Engineering Properties of Commercial Titanium Alloys

TML-19 General Summary of the Physical Metallurgy of Titanium Alloys.

Effect of Hydrogen on the Properties of Titanium and Titanium Alloys (Report in preparation.)

Beta Transformation in Titanium Alloys (Report in preparation.)

Flow Properties, Deformation Textures, and Slip Systems of Titanium and Titanium Alloys. (Report in preparation.)

Welding of Titanium and Titanium Alloys. (Report in preparation.)

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INTRODUCTION

The elements carbon, oxygen, and nitrogen have long been recognized as the most important and most troublesome impurities in titanium. Along with hydrogen*, which much more recently has been found to be an undesirable impurity, they are the only elements which have significant interstitial solubility in titanium. The importance attached to the presence of these interstitial elements is shown by the emphasis placed on them in the few specifications available for titanium and titanium alloys. Paragraph 3.4 of USAF Specification Bulletin No. 108A, dated May 6, 1955, under "Quality Requirements for Wrought Titanium and Titanium Alloys", states: "The following interstitial limits shall be met for all alloys:

Oxygen	0.20% maximum
Nitrogen	0.07% maximum
Carbon	0.20% maximum."

At the June, 1955, ASTM meeting, the committee on titanium accepted the following specifications for titanium sponge:

Nitrogen	0.03 per cent maximum
Carbon	0.05 per cent maximum
Oxygen	Not specified because of analytical difficulties.

There have been many research programs devoted to the study of the effects of interstitials on properties of titanium and its alloys. Numerous other research programs have been directly or indirectly concerned with interstitial content. Results of many of these programs have been published, while results of others are available from research reports. It is the purpose of this report to present the best thoughts on the effects of interstitials on the properties of titanium and its alloys, based on information obtained from the available reports and experience of Battelle staff members. The research on interstitials is continuing, and it must be recognized that the information contained in this report will be subject to modification as new information becomes available.

*The effects of hydrogen on properties of titanium will be covered in detail in a future TML report.

SUMMARY

Carbon, oxygen, and nitrogen are among the chief impurities found in titanium. All three are interstitial solutes which dissolve preferentially in the alpha phase. Like most impurities in metals, they have certain virtues and certain drawbacks. Also like most impurities in metals, they are difficult to remove and must be lived with.

The interstitials offer a substantial strengthening effect with little loss in tensile ductility. However, the interstitials have a very deleterious effect on toughness and notch sensitivity. They increase the strain-rate sensitivity of titanium and produce yield-point phenomena. They lose their strengthening effect at elevated temperatures and promote subzero embrittlement. They cause weld embrittlement and decrease machinability. They make forming operations more difficult by decreasing uniform elongation and decreasing bend ductility. In combination with hydrogen, their detrimental effects are magnified.

The effects of the interstitials are progressive, so that there is no sharp line of interstitial content which separates good properties and poor properties. Also, the effects of the interstitials are additive in direct proportion to their strengthening effect in the alloy base. For example, in unalloyed titanium, 0.1 per cent nitrogen is equivalent to 0.2 per cent oxygen or 0.3 per cent carbon. Thus, the sum of the three interstitials can be expressed in an oxygen equivalency as follows:

$$\text{oxygen equivalent} = \%O + 2 \times \%N + 2/3 \times \%C.$$

The maximum interstitial content tolerable in an alloy will depend on the use to which the alloy will be put. If tensile strength and ductility are the criteria, then an alloy will have a much higher tolerance for the interstitials than if toughness, notch sensitivity, weldability, or other criteria are used. Ideally, the interstitial content should be kept as low as possible and definitely within the maximum limits set in specifications, which are:

Oxygen	0.20 per cent maximum
Nitrogen	0.07 per cent maximum
Carbon	0.20 per cent maximum.

Even here, if all three elements were present in maximum quantity, this would be equivalent to 0.47 per cent oxygen, which is definitely too high for alloys and most uses of unalloyed titanium. Fortunately, most of the titanium being produced today has a hardness of 165 Bhn or less. Sponge having a hardness of 165 Bhn has an interstitial content equivalent to about 0.16 per cent oxygen, which is satisfactory for practically all applications.

In instances where the strength of an alloy or unalloyed titanium is too low because of the use of high-purity sponge, it is possible to use substitutional alpha solutes such as aluminum or tin to augment the strength rather than intentional interstitial additions. Aluminum or tin additions are not detrimental to toughness, notch sensitivity, weldability, and other properties which are deleteriously affected by interstitials.

BASIC PROPERTIES

Phase Relations of Ti-C, Ti-O, Ti-N Alloys

Carbon, oxygen, and nitrogen are classed as alpha stabilizers in titanium terminology. Alpha stabilizers are elements which, when alloyed with titanium, prefer to dissolve in alpha titanium and raise the transformation temperature of titanium. Both oxygen and nitrogen have extensive solubilities in alpha titanium and raise the transformation temperature to such an extent that alpha phase is formed directly from the melt at high oxygen or nitrogen contents. Carbon, on the other hand, has a very limited solubility in alpha titanium and forms a peritectoid system. The titanium-rich portions of the phase diagrams of each of these three systems are shown in Figure 1. (1, 2, 3)* More-detailed diagrams showing the effects of the three interstitials on the transformation temperature and melting point of titanium are shown in Figure 2.

All three elements increase the c/a ratio of the hexagonal-close-packed alpha phase, as shown by the lattice parameters given in Figure 3. It has been hypothesized that the poor fabricability of high-oxygen- and/or nitrogen-containing titanium is caused by the reduction in the number of slip and twinning systems available for flow as the c/a ratio approaches ideal (1.633). (4) A maximum allowable limit of 1.595 (c/a ratio) has been suggested for the maintaining good hot fabricability. (5)

Combinations of carbon, oxygen, and nitrogen are not additive in their effects on the transformation temperature. Combinations of oxygen and nitrogen extend the alpha-beta field to higher total alloy contents at a given temperature than occurs for either binary system. Combinations of carbon and nitrogen or carbon and oxygen result in ternary systems containing a three-phase ($\alpha + \beta + \gamma$) field at high alloy contents. The solubility of carbon in alpha increases with increasing nitrogen or oxygen contents. These effects are illustrated by the isothermal sections of the ternary diagrams shown in Figures 4 and 5. (6)

*References are listed in Appendix C, page C-1. Additional material is listed in the Bibliography in Appendix B, page B-1.

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FIGURE 1. TITANIUM-RICH SYSTEMS Ti-C, Ti-N, AND Ti-O

N-25025

FIGURE 2. EFFECT OF CARBON, NITROGEN, AND OXYGEN ON THE TRANSFORMATION TEMPERATURE AND MELTING POINT OF TITANIUM

FIGURE 3. EFFECT OF CARBON, NITROGEN, AND OXYGEN ON THE LATTICE PARAMETERS OF TITANIUM

A-16300

a. Ti-C-O

b. Ti-C-N

c. Ti-O-N

FIGURE 4. ISOTHERMAL SECTION AT 1000 C OF THE TITANIUM-RICH PORTIONS OF THE Ti-C-O, Ti-C-N, AND Ti-O-N DIAGRAMS

A-16309

617 011

FIGURE 5. EFFECT OF OXYGEN AND NITROGEN ON THE SOLUBILITY OF CARBON IN ALPHA TITANIUM AT 800 C

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Effect of Interstitials on the Phase
Relations of Titanium-Base Alloys

Although considerable research has been done on the determination of ternary titanium-base phase diagrams of systems containing an interstitial element, little work has been done on the temperature ranges of interest in commercial alloys. Specifically, the effects of small amounts of the interstitials on phase relations have not been covered in sufficient detail. Thus, at this time, it is necessary to consider the effects of interstitials on phase relations in a general way rather than to give specific details.

In alpha alloys, additions of oxygen and nitrogen raise the alpha transus and beta transus in conformity with expectations from the binary diagrams. This is illustrated for the Ti-Al-O and Ti-Al-N alloys in Figure 6. (7) The beta transus is raised much more rapidly by the presence of interstitials than is the alpha transus. Carbon has a limited solubility in Ti-Al alloys just as it has in titanium. The solubility of carbon in alpha increases with increasing aluminum content, particularly at temperatures near the peritectoid. The low-temperature (600 C and below) solubility of carbon in titanium is not affected appreciably by aluminum contents up to 8 per cent.

In alpha-beta alloys, the questions of interest are:

- (1) What effect do the interstitials have on the beta transus?
- (2) What is the solubility of the interstitials in beta?
- (3) How does the solubility of the interstitials in beta vary with beta-stabilizing content?
- (4) How do the interstitials partition between the alpha and beta phases in a two-phase alloy?

The general effects of nitrogen and oxygen are to raise the beta transus approximately 50 C for each 0.1 per cent nitrogen and 40 C for each 0.1 per cent oxygen addition in the range of 4 to 8 per cent beta-stabilizer content. This is shown in Figure 7a for nitrogen additions to Ti-Cr alloys⁽⁸⁾ and oxygen additions to Ti-Mn alloys⁽⁹⁾. These data are again approximate and should be used only as a guide.

It has been fairly well established that the solubilities of the interstitial elements in beta-stabilized beta phase increase with increasing temperature in the general form shown in Figure 7b. However, there are only limited data on the effects of beta-stabilizer content on the solubility of the interstitials in the beta phase. Most of the ternary diagrams^(10, 11) indicate that the solubilities of oxygen and nitrogen decrease with increasing beta-stabilizer content in isothermal sections above 1000 C. Little data are

FIGURE 6. EFFECT OF INTERSTITIAL CONTENT ON THE PHASE-TRANSFORMATION TEMPERATURES OF A Ti-4Al ALLOY

A-16310

a. Effect of Small Interstitial Additions on the Beta Transus of Ti-Cr and Ti-Mn Alloys

b. Solubility of Nitrogen in a Ti-6 Cr Alloy, and Oxygen in a Ti-10 Mn Alloy

FIGURE 7. INTERSTITIAL SOLUBILITY IN BETA-STABILIZED TITANIUM ALLOYS

A-16311

available for temperatures in the range of 600 to 800 C, which is the range of interest in the heat treatment of titanium alloys. The two general observations which are most important with respect to the solubilities of interstitials in the beta-stabilized beta phase are:

- (1) The solubility decreases with decreasing temperature.
- (2) The solubility decreases with increasing beta-stabilizer content.

When one considers the phase relations of a ternary system in light of current theory, it is seen that Observation (2) is valid only at temperatures above the transformation temperature of titanium. Below the transformation temperature of titanium, where a two-phase alpha-beta field exists in the binary Ti-(beta stabilizer) system, the solubility in the beta phase must increase with increasing beta-stabilizer content up to the point where a three-phase field exists. The increase in solubility probably is very slight and, for most systems, can be considered insignificant.

In an alpha-beta alloy annealed in the alpha-beta field, it generally is assumed that the interstitials will partition to the alpha phase, leaving the beta phase relatively free of the interstitials. This assumption appears quite valid. Using the Ti-Fe-O system to illustrate this effect, three isothermal sections are shown in Figures 8 and 9⁽¹²⁾. First, it can be seen that the solubility of oxygen in the beta phase is quite low (about 0.1 per cent) at 650 to 900 C, while in alpha, it is very high. The lines connecting the alpha and beta phases show how oxygen is distributed between the two phases at each of the temperatures. The quantity of alpha phase in a given alloy will increase as the annealing temperature is decreased. Also, the quantity of oxygen in the alpha phase will decrease as the annealing temperature is decreased and the quantity of alpha is increased. This can be illustrated by a Ti-3Fe-0.5 O alloy. At the various temperatures, the approximate distribution of oxygen and iron between the two phases can be obtained from the ternary diagram as follows:

Temp. C	Alpha Phase			Beta Phase		
	Quantity, per cent	Composition, per cent		Quantity, per cent	Composition, per cent	
		Oxygen	Iron		Oxygen	Iron
900	20	2.1	0.1	80	0.1 ^(a)	3.5
800	50	0.9	0.1	50	0.1 ^(a)	5
650	80	0.6	0.1	20	0.1 ^(a)	11

(a) Estimated from available phase diagram. It is believed that the actual solubility of oxygen in beta will decrease with decreasing temperatures.

These data have to be regarded as approximate because the solubility of oxygen in beta-stabilized alloys has not been determined precisely. However, they do illustrate how the interstitials are partitioned in an alpha-beta alloy.

FIGURE 8. ISOTHERMAL SECTIONS OF THE TITANIUM-RICH CORNER OF THE TI-Fe-O SYSTEMS

N-25019

FIGURE 9. ISOTHERMAL SECTION OF THE TITANIUM-RICH CORNER OF THE Ti-Fe-O SYSTEMS AT 650 C

A-16312

This partitioning effect is helpful in keeping the interstitials low in the beta phase during alpha-beta solution treatments. However, as the beta-to-alpha ratio increases the amount of interstitial content in the beta will increase also, and have an important effect on the properties of the solution-treated alloy and on the aging response.

Effect of Interstitials on the Beta-Transformation Kinetics*

Most of the data available on the effects of interstitials on the transformation kinetics of the beta phase deal with isothermal transformations. The chief effect is that the interstitials increase the rate of alpha formation from beta by nucleation and growth. A typical example of this effect is shown for a Ti-11Mo alloy containing two levels of oxygen in Figure 10. (13) Increasing the oxygen content in the alloy from 0.02 to 0.15 per cent greatly decreases the time required for initiation and completion of the beta-to-alpha reaction. Similarly, the presence of interstitials in beta phase increases the rate of formation of omega from beta. Indirect evidence from hardness measurements has shown that omega formation can be obtained during quenching of some alloys from the beta field. It also has been shown that increasing the interstitial content increases the tendency to form omega during quenching.

As discussed previously, the beta-phase component of an alloy annealed in the alpha-beta field is generally low in interstitials because of the gettering action of the alpha phase. Thus, it would be expected that isothermal treatments originating from a solution-annealing temperature in the alpha-beta field would not be affected to as great an extent by minor variations in the interstitial content of the alloy as are the treatments originating in the beta field.

In most commercial titanium-base alloys containing beta-eutectoid element(s), the eutectoid reaction is very sluggish. While no conclusive data are yet available, it is believed that the presence of interstitials increases the rate at which the eutectoid reaction occurs in the same manner as it increases the rate of alpha formation from beta.

Diffusion of Interstitials in Titanium

The diffusion rates of carbon and nitrogen in alpha titanium, and of carbon, oxygen, and nitrogen in beta titanium have been determined. Also, the diffusion rate of oxygen in alpha titanium has been calculated, using results of internal-friction measurements. The temperature dependency of

*The subject of transformation kinetics will be covered in more detail in a future TML Report.

FIGURE 10. TTT CURVES FOR Ti-11 Mo ALLOYS CONTAINING TWO LEVELS OF OXYGEN

N-25015

the diffusion coefficients for the three interstitials is given in Figure 11, and a summary of the diffusion constants is given below:

<u>Element</u>	<u>Titanium Modification</u>	<u>Diffusivity Constant, D_0, cm^2/sec</u>	<u>Activation Energy, Q, cal/mol</u>	<u>Reference</u>
Carbon	Alpha	5.06	43,500	14
Carbon	Beta	108	48,400	14
Oxygen	Alpha	0.4	48,000	15
Oxygen	Beta	1.6	48,200	16
Nitrogen	Alpha	1.2×10^{-2}	45,250	16
Nitrogen	Beta	3.5×10^{-2}	33,800	16

EFFECT OF INTERSTITIALS ON THE MECHANICAL PROPERTIES OF UNALLOYED TITANIUM

The effects of the interstitial elements on mechanical properties of titanium can be summarized briefly. They increase the strength at a sacrifice in ductility and toughness of titanium. However, such a statement is too general and needs a great deal of amplification to be meaningful. Thus, this section of the report will deal with the specific effects of the three interstitials, singly and in combination, on the mechanical properties of titanium.

Hardness and Tensile Properties

Hardness and tensile properties are the easiest properties to obtain and, therefore, are the most abundant in the literature. Most of the researches are in good agreement, and results check out very well.

Figure 12a shows the effect of each of the three interstitials on the tensile properties of iodide titanium. (17, 18, 19, 20, 21) It can be seen that nitrogen is the most potent strengthener, followed by oxygen and carbon, respectively. Carbon is effective as a strengthener only up to its limit of solubility in alpha. Above this limit, carbon, present as TiC , does not have much of a strengthening effect. Ductility decreases with increasing interstitial content. Strengthening by oxygen or nitrogen is not a linear function with composition but, rather, follows a parabolic curve. However, in the composition ranges normally encountered in titanium production (up to 0.2 per cent each), the strengthening effects can be considered linear. The strengthening effect of each element can be defined numerically as given on page 20.

FIGURE 11. DIFFUSION COEFFICIENTS FOR THE DIFFUSION OF CARBON, OXYGEN, AND NITROGEN IN ALPHA AND BETA TITANIUM

A-16301

a.

b.

FIGURE 12. EFFECT OF CARBON, OXYGEN, AND NITROGEN ON THE TENSILE PROPERTIES OF IODIDE TITANIUM

N-25012

Element	Increase in Strength	
	Per 0.01 Per Cent, psi	Per 0.1 Per Cent, psi
Nitrogen	3500	35,000
Oxygen	1750	17,500
Carbon	1000	10,000

A good approximation is that 0.03 per cent carbon, 0.02 per cent oxygen, or 0.01 per cent nitrogen provides about the same strengthening effect. This approximation holds true for low quantities of carbon only. In terms of an oxygen equivalency, the interstitials can be grouped as follows:

$$2/3 \text{ C} + 2\text{N} + \text{O} = \text{oxygen equivalent.}$$

Using this relation, the strengths and ductilities of the three systems have been plotted in Figure 12b, where it is seen that the curves for the three systems superimpose very well. Above about 0.15 per cent carbon, the carbon curve deviates because of the formation of TiC. The ductility curves (reduction in area) also superimpose except for the carbon curve at high carbon contents. There is always considerable scatter in ductility values, but an approximation of the loss in ductility caused by the interstitials is shown below:

Element	Loss in Reduction in Area, per cent	
	0.01 Per Cent Addition	0.1 Per Cent Addition
Nitrogen	1.8	18
Oxygen	0.9	9
Carbon	0.4	4

Hardness has been adopted as a measure of sponge quality because of the direct relationship of interstitial content to hardness and the difficulties encountered in obtaining precise analyses, particularly for oxygen. It has not been until recently that specifications have been published stipulating maximum interstitial contents for wrought products. As a result most of the data on sponge quality are based on hardness rather than on complete analyses of the material.

Hardness is a reasonable measure of quality of sponge because it is a measure of the combined interstitial content. However, since the contribution of each of the interstitials to the strength of titanium is different, no correlation of hardness with a single value of total interstitial content can be obtained. Rather, there are numerous combinations of the interstitials of different total interstitial content which will result in the same hardness. The effects of each of the three interstitials on the hardness of iodide titanium is shown in Figure 13. The hardening effect of each of the interstitials follows the same trends as noted for their strengthening effects. That is, about 0.3 per cent carbon, 0.2 per cent oxygen, or 0.1 per cent nitrogen provide about the same hardening effect. As for strength, the oxygen equivalency of:

FIGURE 13. EFFECT OF CARBON, OXYGEN, AND NITROGEN ON THE VICKERS HARDNESS OF IODIDE TITANIUM

A-16299

$$2/3C + 2N + O = \text{oxygen equivalent}$$

can be used to approximate the hardness of titanium.

It would be desirable to correlate hardness with interstitial content expressed in terms of an oxygen equivalent. Assuming that the 2/3:1:2 ratio of effectiveness of carbon, oxygen, and nitrogen is valid over the composition ranges of interest and that hardness is a parabolic function of composition, the following empirical equation can be developed:

$$\text{VHN} = 65 + 310 \sqrt{O_e} \quad , \quad (1)$$

where

$$O_e = \text{oxygen equivalent} = 2/3 \times \text{per cent carbon} + \text{per cent oxygen} + 2 \times \text{per cent nitrogen.}$$

This equation provides a good approximation of the hardening effect of the interstitials added singly or in combination to iodide titanium as shown in Figure 14. Data available from a few lots of completely analyzed sponge titanium also fit this equation very well. Of course, in sponge titanium other elements present as impurities such as iron will affect hardness. One proposed equation⁽²²⁾ that takes into account the effect of iron as well as the interstitial elements is:

$$\text{Bhn} = 35 \sqrt{\% C} + 156 \sqrt{\% O} + 207 \sqrt{\% N} + 12 \sqrt{\% Fe} + 63 \quad . \quad (2)$$

Almost all of the investigations of hardness of titanium as affected by interstitial content have used Vickers hardness data while quality control of sponge and specifications use Brinell hardness numbers. The two hardness scales are approximately parallel, but the Brinell hardness numbers are about 25 points below the equivalent Vickers hardness number. Thus, Equation (1) can be converted from VHN to Bhn as follows:

$$\text{Bhn} = \text{VHN} - 25 = 40 + 310 \sqrt{O_e} \quad . \quad (3)$$

Since most quality control of sponge is based on hardness, it is desirable to be able to calculate the interstitial content from the hardness. Equation (3) then becomes:

$$O_e = \left(\frac{\text{Bhn} - 40}{310} \right)^2 \quad . \quad (4)$$

Using this equation, the oxygen equivalents can be calculated for the various grades of sponge as given on page 24.

FIGURE 14. EFFECT OF TOTAL INTERSTITIAL CONTENT, EXPRESSED IN TERMS OF AN OXYGEN EQUIVALENT, ON THE HARDNESS OF TITANIUM

Oxygen equivalent equals $\frac{2}{3}$ (per cent carbon) + (per cent oxygen) + 2 (per cent nitrogen).

A-16313

<u>Bhn</u>	<u>Calculated Oxygen Equivalent, per cent</u>
125	0.075
145	0.115
165	0.165
185	0.220
205	0.285

Some available data on analyzed sponge give the following results:

<u>Sponge Analysis, per cent</u>			<u>Bhn</u>			
<u>C</u>	<u>O</u>	<u>N</u>	<u>Oxygen Equivalent</u>	<u>Measured</u>	<u>Calculated From Equation (3)</u>	<u>Reference</u>
0.03	0.10	0.014	0.148	150	159	40

Toughness

The most detrimental effect of interstitials is on toughness. High-purity titanium has excellent impact resistance at all temperatures down to at least -196 C. The presence of the interstitials lowers the impact resistance progressively with increasing interstitial content until transition-type behavior occurs. (20, 21) This is illustrated in Figure 15. The effects of combinations of interstitials on toughness appear to be additive on the same basis as their effects on strength ($3C = 2O = 1N$). A tendency toward transition-type behavior occurs at 0.24 per cent oxygen equivalent, and definite transition behavior occurs at 0.36 per cent oxygen equivalent.

In addition to affecting notch-bar toughness, the interstitial elements appear to cause a temperature dependency on other ductility parameters. Notched and unnotched tensile ductilities undergo an apparent transition from ductile to brittle behavior. The transition temperature or temperature range is increased with increasing interstitial content.

Temperature Dependency of Mechanical Properties

Strengths of materials generally decrease with increasing temperature. The rate of decrease varies with the composition of the material. In titanium and titanium alloys, the interstitial elements provide a significant strength increase at room temperature, but their effectiveness decreases as the temperature is increased. (23) This is illustrated in Figure 16. It can be seen that most of the strength advantage gained from interstitial content is lost at temperatures of 400 C (750 F) and above. Similarly, other strength-dependent properties show the same type of decrease at elevated

FIGURE 15. EFFECT OF INTERSTITIALS ON THE TOUGHNESS OF IODIDE TITANIUM

N-25028

FIGURE 16. EFFECT OF TEMPERATURE ON THE TENSILE PROPERTIES OF TITANIUM CONTAINING SEVERAL LEVELS OF INTERSTITIAL ELEMENTS

N-25017

temperatures. Stress-rupture and creep properties, like tensile strength, decrease more rapidly with increasing temperature for interstitial-strengthened titanium than for unalloyed titanium. In stress-rupture properties this effect would be expected to show up as a more rapid loss in rupture strength with time at a given testing temperature. The data given in Figure 17⁽²⁴⁾ illustrate the ineffectiveness of oxygen as a strengthener in stress-rupture properties. At 1000 F, 0.3 per cent oxygen maintains its strengthening effect, but 0.15 per cent oxygen loses its effectiveness with increasing time. At 1200 F, the presence of 0.15 per cent oxygen in titanium does not cause any significant increase in stress-rupture strength over unalloyed titanium. The 0.3 per cent oxygen addition which caused a considerable strength increase at 1000 F is much less effective at 1200 F. Also, as for the 0.15 per cent oxygen alloy at 1000 F, the loss in strength with time is much greater for the 0.30 per cent oxygen alloy at 1200 F.

Similar effects would be expected in creep properties where the advantage in increased creep resistance obtained at room temperature by strengthening titanium with interstitials would be progressively lost as the testing or service temperature is increased. Indirect evidence supporting this expectation is shown in Figure 18, where the stress to produce 1 per cent total creep in 100 hours is plotted against testing temperature for two grades of unalloyed titanium.⁽²⁵⁾

At temperatures below room temperature, the slope of the temperature-strength curve remains high for high-interstitial-content titanium, and sub-zero embrittlement is encountered. The temperature at which embrittlement occurs increases as the interstitial content is increased, as is illustrated in Figure 19. The presence of a notch produces embrittlement at somewhat higher temperatures, and when the interstitial content is sufficiently high, room-temperature embrittlement is encountered such as is obtained in the Ti-0.2N alloy in the notched condition shown in Figure 19b.

Strain-Rate Sensitivity and Strain Aging

The strength of titanium is known to be dependent on the rate of straining during a tensile test; the faster the strain rate, the higher is the strength. A detailed investigation of the effects of interstitials and other elements on the strain-rate sensitivity of titanium has been conducted.⁽²⁷⁾ This research has shown that the strain-rate sensitivity of titanium increases with increasing interstitial content, but is not changed by the addition of substitutional alpha solutes, such as aluminum. This is illustrated in Figure 20. The strain-rate sensitivity in Kroll-type titanium is found to be most pronounced in the temperature range of 25 to 125 C, as shown in Figure 21.⁽²⁸⁾ Yield points were noted in samples tested at both slow (0.003/min) and fast (0.138/min) strain rates at temperatures of 115 to 280 C with maximum effect at 230 C. Aging at 200 C after a 5 per cent prestrain resulted in the appearance of a yield point and an increase in

FIGURE 17. STRESS - RUPTURE CURVES FOR Ti-O ALLOYS AT 1000 F AND 1200 F

N-25024

FIGURE 18. STRESS TO PRODUCE 1 PER CENT TOTAL CREEP IN 100 HOURS IN TWO GRADES OF UNALLOYED TITANIUM N-25018

a. Unnotched Tensile Strength

b. Notched Tensile Strength

FIGURE 19. EFFECT OF TEMPERATURE ON THE NOTCHED AND UNNOTCHED TENSILE STRENGTH OF TITANIUM CONTAINING INTERSTITIALS

Data from Reference (25).

FIGURE 20. YIELD STRENGTH VERSUS STRAIN RATE
AT ROOM TEMPERATURE

N - 25030

817 035

FIGURE 21. EFFECT OF TEMPERATURE AND STRAIN RATE ON THE YIELD STRENGTH OF TITANIUM

A-16302

strength at room temperature. These observations were taken as evidence that strain aging occurs in titanium and that the interstitials might be responsible for this behavior.

The yield-point phenomenon at room temperature has been noted in high-purity titanium alloys containing interstitial elements⁽²⁰⁾ but not in high-purity titanium or alpha alloys containing only substitutional alpha solutes. This is evidence that the yield point in titanium is caused by the interstitial elements. The yield-point behavior, strain aging, and strain-rate sensitivity may be all related. Precipitation of a second phase appears out of the question because of the high solubility of the interstitials in titanium. It is possible that the solute atoms (interstitial atoms) segregate to preferred sites, possibly dislocations. If such is the case, then slow-strain-rate tests would permit movement of the solute atoms from preferred locations during the test, resulting in lower flow stresses. Yield-point phenomena in other metals have been related to the clustering of interstitials at dislocations, and it is very probable that this is the mechanism operative in titanium.

EFFECT OF INTERSTITIALS ON THE MECHANICAL PROPERTIES OF TITANIUM ALLOYS

The effects of interstitials on the properties of titanium alloys are similar to their effects on unalloyed titanium. However, the magnitude of the effects will vary, depending upon the alloying elements present in the alloy. Similarly, the tolerances for interstitials will vary with the alloy composition, and specific tolerances should be established for each alloy or type of alloy. In the discussion that follows, the effects of interstitials on the properties of the different alloy types are discussed in each property section.

Tensile Properties

The equivalency of the strengthening effect of the interstitials for unalloyed titanium ($3C = 2O = 1N$) does not apply to alpha alloys strengthened by the substitutional solutes, aluminum and tin. Nitrogen is still the most potent strengthener, but its strengthening effect varies with aluminum or tin content. In Ti-Al alloys, carbon becomes a greater strengthener than oxygen, while in Ti-Sn alloys, oxygen is a greater strengthener than carbon. Data on high-purity alloys showing these effects are given in Figure 22. (29, 30). With respect to ductility, nitrogen in Ti-Al alloys causes a rapid decrease in ductility, while oxygen and carbon in small amounts do not impair ductility. In Ti-Sn alloys, the strengthening effects of all three interstitials are much less than in Ti-Al alloys or unalloyed

FIGURE 22. EFFECT OF INTERSTITIAL CONTENT ON THE TENSILE PROPERTIES OF ALPHA ALLOYS

N-25096

titanium, and the ductilities are not significantly affected. This indicates that Ti-Sn alloys may have a much higher tolerance for the interstitial elements than Ti-Al alloys.

The role of interstitials in alpha-beta alloys is more complex than in the single-phase alpha alloys because of the partition of the interstitials to the alpha phase. Because of this partition the interstitials strengthen the alpha phase much more than the beta phase. Thus, the effectiveness of the interstitials in strengthening alpha-beta alloys will be dependent on the quantity and composition of the two phases. Alpha-beta alloys can be classified in several ways. For this discussion it is best to classify them according to substitutional alloy content and microstructure as follows:

Type of Alpha-Beta Alloy	Alloy Content	Annealed Microstructure
Lean beta	2 to 5 per cent beta solutes	Predominantly alpha phase with beta in the grain boundaries, 60 per cent or more alpha
Rich beta	6 to 9 per cent beta solutes	Predominantly beta-phase matrix, 50 per cent or more beta
Aluminum-enriched lean-beta alloy	2 to 5 per cent beta solutes, 3 to 6 per cent aluminum	Same as lean beta, 60 per cent or more alpha

In lean-beta alpha-beta alloys it would be expected that the interstitials would have a significant strengthening effect because the alpha phase is the predominant phase in these alloys. Examples of this effect are shown in Figure 23 for three binary lean beta alloys.⁽³¹⁾ It can be seen that a marked strength increase is obtained with increasing interstitial content in the Ti-3Fe and Ti-3Mn alloys. In the Ti-3V alloy a lower strengthening effect is obtained by the addition of interstitials. This may be an effect of the alpha solubility of vanadium which is much higher than that of manganese or iron.

In annealed rich-beta alloys it would be expected that the interstitials would have less effect on strength than in annealed lean-beta alpha-beta alloys because of the low interstitial solubility in the beta phase. In the annealed condition, the interstitials partition to the alpha phase which is the minor phase. Thus, increasing the interstitial content of the alloy would increase the interstitial content of the alpha phase greatly with only a small increase in the interstitial content of the beta phase. Since the strength of rich-beta alloys is dependent primarily on the strength of the matrix phase (beta), increasing the interstitial content of the alloy should have only a small effect on strength. Few data are available on specific effects of interstitials on rich-beta alloys, particularly in the annealed

of

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FIGURE 23. EFFECT OF CARBON, OXYGEN, AND NITROGEN ON THE TENSILE PROPERTIES OF LEAN BETA ALLOYS

N-25016

condition. Some data from a heat-treatment study of a Ti-7Mn alloy⁽³²⁾ do illustrate this effect as shown in Figure 24. In the beta-furnace-cooled condition, which may be considered equivalent to an annealed condition, it is seen that the interstitials have a much lower strengthening effect than was found for a lean-beta alloy, such as the Ti-3Mn alloy.

In heat treatments of alpha-beta alloys the interstitials affect reaction rates as well as affecting the properties of two phases. It is known that the interstitials in solution in the beta phase increase the rates of beta-phase transformation reactions. Thus, the tensile properties of heat-treated alpha-beta alloys containing interstitials will be affected by the effect of interstitials on reaction rates and on properties of the two phases. In the present state of the art, it is not possible to separate these two effects. The data given in Figure 24 show that nitrogen additions provide a much greater strengthening effect than oxygen or carbon additions in a quenched-and-aged Ti-7Mn alloy. Undoubtedly both effects play an important part here, but additional research is needed before a sound technical explanation can be given.

In aluminum-enriched lean-beta alpha-beta alloys, it would be expected that the interstitials would have the same effect on tensile properties as they have on plain lean-beta alloys. This is shown in Figure 25 for interstitial additions to an iodide titanium base Ti-5Al-2.5Mo alloy.⁽³³⁾ It is interesting to note that all three interstitials have about the same strengthening effect in this alloy.

It has been shown previously that the increase in room-temperature strength caused by interstitials in unalloyed titanium decreases with increasing temperature. In titanium alloys, it would be expected that the same type of behavior would occur. However, since the alloying additions to titanium increase the recovery and recrystallization temperatures of titanium, the temperatures at which the effectiveness of the interstitials is lost would be higher in alloys than in unalloyed titanium. Alloys containing aluminum have the highest recovery and recrystallization temperatures. Thus, it would be expected that the interstitials in alpha Ti-Al alloys and aluminum-enriched alpha-beta alloys would have strengthening effects at higher temperatures than in aluminum-free alloys. Data on the effect of temperature on properties of Ti-Al alloys containing oxygen are shown in Figure 26⁽³⁴⁾ and on Ti-4Al-4Mn alloys containing oxygen in Figure 27.⁽²²⁾

The interstitials also increase the notch sensitivity of titanium alloys in tensile tests. Generally, the notched tensile strength of a material is higher than the unnotched tensile strength. When the notched tensile strength is lower than the unnotched strength it is an indication of extreme embrittlement. The temperature at which embrittlement occurs is very important. The higher the transition temperature (transition from ductile to brittle behavior), the more susceptible an alloy is to embrittlement. In

FIGURE 24. EFFECT OF C, O, AND N ON THE TENSILE PROPERTIES OF A Ti-7Mn ALLOY IN TWO HEAT-TREATED CONDITIONS

N-25027

FIGURE 25. EFFECT OF INTERSTITIAL CONTENT ON THE TENSILE PROPERTIES OF A Ti-5Al-2.5Mo ALLOY IN THE ANNEALED CONDITION

N-25023

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FIGURE 26. EFFECT OF OXYGEN CONTENT ON THE ELEVATED-TEMPERATURE TENSILE PROPERTIES OF C-130AM (Ti - 4Al - 4Mn) N-25013

FIGURE 27. EFFECT OF TEMPERATURE ON THE TENSILE STRENGTH OF TITANIUM AND A Ti-4Al ALLOY WITH AND WITHOUT AN 0.2 PER CENT OXYGEN ADDITION

N-25020

a research investigation being conducted at Syracuse University⁽²⁶⁾ the effects of interstitials on the notched tensile strength of titanium alloys are being studied. In this study the ratio of notched tensile strength to the room temperature unnotched tensile strength is used as a measure of notch sensitivity. For notch-insensitive material, this ratio will increase uniformly with decreasing temperature. For material which is notch sensitive the temperature at which this ratio changes and starts to decrease can be taken as the transition temperature. Some preliminary results from this investigation are shown in Figure 28. These results indicate that the interstitials have a detrimental effect on notch sensitivity. The additional studies now in progress on this investigation should aid greatly in the understanding of the effects of interstitials on notch sensitivity of titanium alloys.

Toughness

The interstitial elements carbon, oxygen, and nitrogen are detrimental to the impact resistance in titanium alloys, as they are to unalloyed titanium. The tolerance for the interstitials while maintaining good toughness is somewhat less for alloys than for unalloyed titanium, because the substitutional alloying additions themselves lower impact resistance to some extent. Examples of the loss of notch toughness caused by the interstitials in titanium alloys are given in Figures 29, 30, and 31.

Creep and Stress Rupture

No data have been found on the effects of interstitials on the creep and stress-rupture properties of titanium alloys. Creep and stress-rupture properties, like elevated-temperature strengths, can be expected to be dependent more on the base composition of an alloy than on the interstitial content. Thus, any advantages gained from the interstitials at room temperature may be lost at elevated temperatures.

Fatigue

The effects of the interstitials on the fatigue behavior of titanium and titanium alloys are not too well understood at this time. Fatigue properties are dependent on many mechanical variables as well as on compositional or structural variables. Surface condition, notch dimensions, and type of fatigue test have a great influence on the fatigue strength of an alloy. Thus, minor variations in fatigue properties may be equally attributable to differences in test conditions and differences in interstitial content.

FIGURE 28. EFFECT OF TEST TEMPERATURE ON THE NOTCH STRENGTH-ROOM TEMPERATURE TENSILE STRENGTH RATIO OF SEVERAL TITANIUM ALLOYS

N-25014

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FIGURE 29. EFFECT OF OXYGEN ON THE CHARPY
IMPACT PROPERTIES OF Ti - 4Al - 4Mn
N-25021

FIGURE 30. EFFECT OF SMALL ADDITIONS OF NITROGEN AND CARBON ON THE TOUGHNESS OF A BETA-QUENCHED Ti-9Mn ALLOY

N-25022

A. Effect of Interstitial Content on the Impact Resistance of A-110 AT (Ti-5Al-2.5Sn) at Room Temperature and -40 F

B. Effect of Interstitial Content on the Impact Resistance at -40 F of a Ti-7Mn Alloy in Two Conditions

FIGURE 31. EFFECT OF INTERSTITIAL ADDITIONS ON THE IMPACT STRENGTHS OF TWO COMMERCIAL ALLOYS AT LOW TEMPERATURES

A summary of the fatigue strengths of several lots of unalloyed titanium and several titanium alloys is given in Table 1. There is a trend of decreasing unnotched fatigue strength with increasing tensile strength (or increasing interstitial content) for unalloyed titanium. However, no definite trend can be obtained from the notched fatigue-strength data. The only data for the alloys that can be compared on the basis of interstitial content are the data for Ti-150A and Ti-175A. These two alloys are basically the same composition except for interstitial content. Ti-175A contains a nominal 0.5 per cent oxygen, while Ti-150A contains a nominal 0.25 per cent oxygen. In the unnotched condition, the Ti-175A alloy has a higher fatigue strength than the Ti-150A alloy, indicating that the increased interstitial content may be beneficial.

In general, it appears that the fatigue properties of titanium and titanium alloys are satisfactory. If, in the future, fatigue becomes a problem in titanium alloys, a research investigation should be undertaken to obtain specific information on the effect of interstitials on the fatigue behavior of alloys of interest.

Stability

Stability is a very important property of alloys to be used in elevated-temperature service. A stable alloy is one which can be used in service for extended periods of time without significant changes in subsequent room-temperature properties. Instability shows up as changes in mechanical properties resulting from reactions which occur during service. Alpha alloys, being single phase, are not subject to transformation reactions during service and are stable. The beta phase of alpha-beta alloys can decompose during service, resulting in mechanical-property changes. Thus, alpha-beta alloys are prone to instability.

The effects of carbon, oxygen, and nitrogen on the stability of alpha-beta alloys are directly related to their effects on beta-decomposition reaction kinetics. It is known that interstitial elements dissolved in the beta phase increase the rate of formation of alpha (and omega) from beta, indicating that their presence would be detrimental to stability. This is true for single-phase beta alloys or beta-quenched alpha-beta alloys. However, when alpha-beta alloys are fully annealed (or stabilized), the interstitials partition predominantly to the alpha phase, leaving the beta phase relatively free of interstitials.

Considering the effects of interstitials on ternary equilibria, it can be seen that the phase relations of an alpha-beta alloy are greatly affected by the interstitials. For a given annealing temperature, the ratio of alpha to beta in an alpha-beta alloy will increase with increasing interstitial content. Also, the beta-stabilizer content of the beta phase will increase with increasing interstitial content. Referring to Figure 8 (Ti-Fe-O system), the distribution of the phases present in a Ti-3Fe alloy solution annealed at 800 C changes with increasing oxygen content approximately as given on page 49.

TABLE 1. FATIGUE-ENDURANCE LIMITS FOR SEVERAL
GRADES OF UNALLOYED TITANIUM AND
SEVERAL TITANIUM ALLOYS

(Rotating-Beam Fatigue Tests)

Material	Unnotched Tensile Strength, 1000 psi	Fatigue Strength at 10^7 Cycles, 1000 psi		Reference
		Unnotched	Notched	
Titanium	64	52	27 ($K_T=3$)	38
A-55	71	49	24 ($K_T=3$)	39
A-55	78	48	32 ($K_T=3.48$)	40
Ti-75A	84	42	--	41
A-110AT	121	62	27 ($K_T=3.2$)	42
Ti-8Mn	135	89	37 ($K_T=3$)	39
Ti-150A	138	67	7.5 ($K_T=3.5$)	43
Ti-150A	143	67	23 ($K_T=2.75$)	44
C-130AM	149	67	24 ($K_T=2.65$)	43
Ti-175A	161	87	6.0 ($K_T=3.5$)	44

Oxygen Content, per cent	Alpha Phase		Beta Phase	
	Quantity, per cent	Iron Content, per cent	Quantity, per cent	Iron Content, per cent
0	44	0.1	56	4.6
0.1	46	0.1	54	4.7
0.5	50	0.1	50	5
1.0	70	0.1	30	8.5

This would indicate that, for a given annealing treatment, an alloy with high interstitial content would be more stable than the same alloy with a lower interstitial content, because, in general, an alloy is most stable when the ratio of alpha to beta is higher and the beta-stabilizer content of the beta phase is high.

The above considerations are based on partitioning of interstitials to the alpha phase and effect of interstitials on ternary equilibria. The final proof of such considerations will be dependent on results of mechanical-property studies. So far as is known, there are very few data specifically obtained from a study of the effects of interstitials on the stability of alpha-beta alloys. One investigation which included the study of the stability of a Ti-2.5Mo-2.5Cr-0.1 O alloy as compared to a Ti-2.5Mo-2.5Cr alloy showed no significant differences in the stability of the two alloys.⁽³⁸⁾ This is illustrated by the data shown in Figure 32. Some additional data on aging response of two Ti-Mn alloys is shown in Figure 33.⁽⁴⁵⁾ Here, the instability of the beta phase shows up as an increase in hardness.

In the beta-quenched condition, the alloy containing nitrogen has the greater aging response, whereas, in the 750 C quenched condition, where the alloy containing nitrogen contains much more alpha phase and has a high-manganese-content beta phase, the alloy without nitrogen has the greater hardening response. In the 650 C quenched condition, which may be considered equivalent to an anneal, both alloys show only slight aging response. The alloy without nitrogen ages in less time than the alloy with nitrogen. However, after 64 hours, both alloys have been hardened to about the same extent.

At this time it appears that interstitial elements in annealed alpha-beta alloys will not promote instability, and perhaps, in some instances might even promote stability. However, more research is needed on this subject before the specific effects of the interstitials on stability are known.

FIGURE 32. EFFECT OF AGING TEMPERATURE ON THE ROOM-TEMPERATURE TENSILE PROPERTIES OF A Ti-2.5Mo-2.5Cr ALLOY AND A Ti-2.5 Mo-2.5 Cr-0.1 O ALLOY AGED FOR 200 HOURS

A-16314

FIGURE 33. EFFECT OF AGING TIME AT 400 C ON THE VICKERS HARDNESS OF AN IODIDE BASE Ti-6Mn WITH AND WITHOUT AN 0.1 PER CENT NITROGEN ADDITION

EFFECT OF INTERSTITIALS ON PROCESSING PROCEDURES

Melting

The predominant melting method for titanium and titanium alloys is arc melting (either inert or consumable electrode) in a water-cooled crucible. The interstitial content of the sponge has little effect on the melting characteristics of the sponge. Small quantities of carbon, oxygen, and nitrogen raise the melting point of titanium slightly. Also, there is some tendency for minor compositional (interstitial content) variations to occur during freezing because of the difference in temperature between the liquidus and solidus. High carbon contents cause formation of carbide stringers during freezing. However, the minor segregation that occurs is overcome during subsequent fabrication and annealing treatments. Also, the carbide stringers are broken up during fabrication and appear as uniformly distributed equiaxed carbides in the final structure.

It is most important to have uniform sponge or a uniform mixture of sponge if more than one lot is being melted at one time, so that gross interstitial segregation will not occur. Ingot inhomogeneity will not occur if the sponge used is homogeneous.

The melting operation is one process in which interstitials, particularly oxygen, can be picked up. Contamination during melting can occur from impurities present in the melting atmosphere and adsorbed gases or moisture in the furnace system. Titanium melters are aware of such sources of contamination and have developed techniques to keep such contamination to a minimum.

Primary Fabrication

The effects of interstitials on the forging and rolling of titanium and titanium alloys can be related to their effects on elevated-temperature properties. The strengthening effect of the interstitials decreases with increasing temperature until, at fabrication temperatures (1200 F and above), they have little strengthening effect. However, the interstitials promote strain-rate sensitivity in titanium and, since fabrication operations involve high-strain-rate deformation, some effect of interstitials would be expected. The results of forgeability tests on two grades of unalloyed titanium are shown in Figure 34.⁽⁴⁶⁾ Like tensile strength, there is a tendency for the effect of interstitials to decrease with increasing temperature. Normal variations in interstitial content will not adversely affect the fabricability of titanium and titanium alloys. Also, any interstitial specification established for mechanical properties would be well below the fabricable limit.

FIGURE 34. COMPARATIVE FORGEABILITY OF TWO GRADES OF UNALLOYED TITANIUM

A-16303

Hot fabrication, like melting, is a process in which interstitial contamination can occur, since all primary fabrication is done in air. In addition to the normal oxidation process which scales the metal, a diffusion process occurs whereby oxygen is diffused into the metal at elevated temperatures. Like all diffusion processes, this reaction is time and temperature dependent. The quantity and depth of oxygen diffusion will depend upon these variables. Results of a study⁽⁴⁷⁾ on the effects of time and temperature on the depth of contamination of titanium and two titanium alloys are summarized in the nomographs in Figures 35, 36, and 37. These nomographs are based on parametric equations derived from diffusion data. In each of the following equations, the depth of contamination (x) for any time-temperature combination may be obtained:

<u>Alloy</u>	<u>Equation</u>
Unalloyed Ti (A-55)	$\log x = C' + 0.5 \log t - \frac{10700}{T}$
Ti-5Al-2.5Sn (A-110AT)	$\log x = C' + 0.5 \log t - \frac{6430}{T}$
Ti-4Al-4Mn (C-130 AM)	$\log x = C' + 0.5 \log t - \frac{6050}{T}$

where x is in mils, t is in hours, and T is in degrees Kelvin. The constant, C', varies with degree of contamination and is a function of the hardness change (ΔKHN).

Like all diffusion processes, there is a composition gradient from the oxide/metal interface to the uncontaminated core. Since hardness is a function of oxygen content, the hardness increase over the hardness of the base alloy can be used as a measure of the degree of contamination. Typical hardness-depth curves for unalloyed titanium are shown in Figure 38. The most contamination occurs near the surface. For the times and temperatures involved in fabrication operations, the depth of contamination is generally on the order of a few mils. This can be removed by scalping when working with forgings or plate. However, when working with thin-gage sheet, contamination of a few mils depth becomes a problem, and fabrication conditions must be controlled.

Secondary Fabrication

The interstitial content of titanium and titanium alloys is much more important in secondary fabrication operations than in primary fabrication. Most of the secondary fabrication, such as bending, dimpling, stretching, cupping, and other forming operations, is done cold or at slightly elevated temperatures. Machining and welding are also adversely affected by increasing interstitial content.

Key: Draw a line from ΔKHN to t , mark m .
Draw a line from m to F , read x .

FIGURE 35. FOR ESTIMATING THE DEPTH OF CONTAMINATION OF COMMERCIAL TITANIUM FROM COMBINATIONS OF TIME AND TEMPERATURE OF EXPOSURE TO AIR

This is based on the solution of $\log x = C + 0.5 \log t - \frac{10700}{T}$ and $C = f(\Delta KHN)$.

Note: The temperature, T , in the equation is in degrees Kelvin.

A-12918

FIGURE 36. FOR ESTIMATING THE DEPTH OF CONTAMINATION OF Ti-5Al-2.5Sn FROM COMBINATIONS OF TIME AND TEMPERATURE OF EXPOSURE TO AIR

This is based on the solution of $\log x = C + 0.5 \log t - \frac{6430}{T}$ and $C = f(\Delta KHN)$.

Note: The temperature, T , in the equation is degrees Keloin.

FIGURE 37. FOR ESTIMATING THE DEPTH OF CONTAMINATION OF Ti-4Al-4Mn FROM COMBINATIONS OF TIME AND TEMPERATURE OF EXPOSURE TO AIR

This is based on the solution of $\log t - \frac{6050}{T}$ and $C = f(\Delta KHN)$.

Note: The temperature, T , in the equation is in degrees Kelvin.

FIGURE 38. SUMMARY OF HARDNESS-PENETRATION DATA FOR RC-55, HEATED FOR VARIOUS TIMES IN AIR AT 1600 F

0-22661

Forming Operations

As pointed out by L. R. Jackson in TML Report No. 12, the metal flow during forming may be tension flow or compression flow. Either type of flow may be uniaxial or biaxial, and both types may occur at various stages during a forming operation. Two tests can be used to obtain indications of formability of metals: the tension test in which uniform elongation is measured and the bend test. Uniform elongation is a measure of the ability of a metal to be stretched plastically without undergoing localized deformation. Bend tests are used for sheet material to simulate forming operations. The minimum bend radius is measured and is generally expressed in terms of thickness of the sheet. The minimum bend radius is the smallest radius through which a sample can be bent without cracking.

The presence of interstitial elements decreases the uniform elongation and increases the minimum bend radius in titanium. Examples of the effects of the interstitials on uniform elongation^(19, 20, 38) are given below:

<u>Composition, per cent</u>	<u>Uniform Elongation, per cent</u>
Iodide Ti	35
Ti-0.07 O	14
Ti-0.13 O	12
Ti-0.07N	13
Ti-0.29N	11
Ti-0.16C	14
Ti-0.27C	12
Ti-0.47C	11
Ti-0.19C-0.12 O	9
Ti-0.38C-0.2 O	9
Ti-0.014N-0.03C-0.10 O(a)	16

(a) Unalloyed Kroll-process titanium.

In annealed alpha-beta alloys, the matrix phase (beta) is relatively free of interstitials and the ductility characteristics of the alloys should be similar to the ductility of the beta phase. Examples of the effect of nitrogen on the uniform elongation of some Ti-Mn alloys in the annealed condition^(36, 37) are given below:

<u>Composition, per cent</u>	<u>Uniform Elongation, per cent</u>
Ti-3.4Mn	14
Ti-2.68Mn-0.07N	15
Ti-6.4Mn	13
Ti-5.63Mn-0.11N	13
Ti-9.4Mn	12
Ti-7.92Mn-0.073N	12

These data indicate that the uniform elongation of annealed alpha-beta alloys is dependent more on the beta-stabilizer content than on the interstitial content.

An example of the effects of interstitial content on the bend ductility of titanium is given in Figure 39. Again, it can be seen that the interstitials are detrimental to formability. In addition to affecting bend ductility, the presence of interstitials also affects spring back. The amount of spring back that occurs after a forming operation can be directly related to the yield strength of the material being formed. Since carbon, oxygen, and nitrogen raise the yield strength of titanium, they can be expected to increase spring back. Figure 40 illustrates the increase in spring back caused by interstitials (or increasing yield strength) in titanium.⁽²²⁾ One method of overcoming spring-back is to perform the bending operation at moderately elevated temperatures (up to 1000 F). This procedure has the advantage that the yield strength of titanium is much lower, which reduces spring-back tendencies. Also, if the bending operation is done slowly or the bent member is held in the fixture for a period of time, the spring back will be less because of the creep characteristics of titanium reducing the flow stresses.

Welding

In considering the effects of interstitials on the weldability of titanium, it must be pointed out that it is not the welding process that is affected, but, rather, the subsequent properties of the alloys. The welding characteristics do not change significantly with minor variations in interstitial contents. However, the ductilities of the weld joints are greatly reduced by the presence of interstitials.

In unalloyed titanium, the interstitial content should be kept below the following amounts to avoid brittle welds: carbon, 0.28 per cent; oxygen, 0.15 per cent; and nitrogen, 0.05 per cent.⁽⁴⁸⁾ These values are for single additions to sponge. When more than one interstitial is present, the tolerance would be proportionate to the individual tolerances.

Titanium alpha alloys are the only alloys which are as ductile in the welded condition as they are unwelded. The effects of interstitials on the weld ductility of the alpha alloys are similar to their effects on unalloyed titanium. However, the tolerances have not been established for many alpha alloys. Interstitial limits determined for a Ti-5Al alloy for maintaining ductile welds are 0.20 per cent carbon, 0.18 per cent nitrogen, and 0.25 per cent oxygen.⁽⁴⁹⁾ At this time, it appears that Ti-Sn, Ti-Al, and Ti-Al-Sn alloys can tolerate as much interstitials and maintain ductile welds as unalloyed titanium can.

Most of the alpha-beta alloys become brittle when welded because of freezing segregation and transformation hardening. In composition ranges

FIGURE 39. CORRELATION BETWEEN BRINELL
HARDNESS AND BEND DUCTILITY OF
UNALLOYED TITANIUM⁽²²⁾

A-16304

FIGURE 40. SPRING-BACK OF TITANIUM OF VARIOUS YIELD STRENGTHS VERSUS RATIO OF MATERIAL THICKNESS TO FINAL PART RADIUS

A-16306

where the alloys are weld ductile, small amounts of interstitials cause weld embrittlement. It appears that, to maintain a weldable alpha-beta alloy, the interstitial content should be kept low, as well as the beta-stabilizer content. Of the commercial alpha-beta alloys, only the Ti-6Al-4V and the Ti-1.5Al-3Mn alloys have been reported as being weldable. Even in these alloys, the ductilities of the welds are much less than the ductilities of the bases, and the interstitial content must be kept low to obtain this ductility.

Because the interstitials have such a detrimental effect on weld ductility, it is imperative that the welding of titanium and titanium alloys be conducted in an inert atmosphere. Welding techniques have been developed, using inert-gas trailing shields and backups, which have eliminated or minimized interstitial contamination during welding. In a study of the purity of welding atmospheres⁽⁵³⁾, it was found that as little as 0.25 volume per cent of nitrogen, oxygen, or dry air in the helium atmosphere adversely affected the properties of titanium welds. Impact strengths as well as ductilities were lowered considerably by small percentages of these contaminants.

A detailed description of the welding of titanium alloys will be given in a future TML report.

Machining

The machining characteristics of titanium and titanium alloys are very dependent on interstitial content. A simple rule that appears to hold true is that machining becomes more difficult as the hardness of the alloy is increased⁽⁵¹⁾. This is shown in Figure 41. Since the hardness of an alloy, at least above the base hardness, is a function of the interstitial content, it can generally be stated that the machinability decreases as the interstitial content increases. Carbon is much more detrimental to machinability than the other interstitials, particularly when present in quantities large enough to produce free carbides.

Surface contamination of the type that occurs during primary working makes machining difficult. Since this contaminated layer has to be removed, the recommended heavy-feed, slow-speed machining of billets and bar stock is helpful. By using deep cuts, the tip of the tool is under the contaminated layer in softer metal.

Alloying additions to titanium also increase the hardness, with the result that machinability decreases. Therefore, it is necessary to accept decreased machinability to obtain high-strength alloys.

FIGURE 4I. COMPARATIVE TURNING AND SAWING INDEXES FOR TITANIUM, STAINLESS STEEL, AND A TI-0.47C ALLOY

A-16305

EFFECTS OF COMBINATIONS OF ALPHA-SOLUTE INTERSTITIALS AND HYDROGEN

The characteristics of the alpha-solute interstitials, carbon, oxygen, and nitrogen, are much different from the characteristics of hydrogen, which is a beta-solute interstitial. Consequently, most researches have considered either only the alpha-solute interstitials or only hydrogen because of their great dissimilarity. As a result, there are few data available on the effects of combinations of the two different types of interstitials.

One research investigation has shown that combinations of the two types of interstitials are detrimental to impact. (39) In alpha titanium, carbon, oxygen, and nitrogen in solid solution are very detrimental to impact properties. Hydrogen, on the other hand, is insoluble in alpha titanium at ambient temperatures and is present as hydride particles. The presence of these hydride particles is very detrimental to impact properties. Thus, although their solubilities in alpha titanium are diametrically opposite, the effects of the two types of interstitial elements on impact are similar. Data on the effects of combinations of hydrogen and oxygen on the impact properties of unalloyed titanium are shown in Figure 42. (39)

In alpha Ti-Al alloys, the solubility of hydrogen in alpha titanium is much higher than in unalloyed titanium. Also, it has been found that the tolerance of Ti-Al alloys for hydrogen before the impact resistance is lowered is much higher than for unalloyed titanium. The data in Figure 43 indicate that the combinations of hydrogen and oxygen studied in a Ti-5Al alloy are not any more detrimental than the presence of oxygen alone. It appears that hydrogen in solution is not detrimental to impact properties even in combination with alpha-solute interstitials. However, if present as hydride particles, hydrogen in combination with the alpha-solute interstitials is very detrimental.

The effects of combinations of the two types of interstitials on other mechanical properties have not received extensive study to date. It is known that hydrogen causes embrittlement of some alpha-beta alloys in slow-strain-rate tests. What the effect of alpha solutes in combination with hydrogen in these alloys would be is not known. At this stage of the art, it is best not to attempt to predict such effects. This is an area that should be covered in future researches.

USE OF SUBSTITUTIONAL ALPHA SOLUTES TO REPLACE INTERSTITIAL ELEMENTS

It has been pointed out that the interstitial elements can be used to provide a substantial strength increase in titanium alloys without much detriment to room-temperature ductility. In fact, it is often necessary to

FIGURE 42. EFFECT OF COMBINATIONS OF OXYGEN OR NITROGEN AND HYDROGEN ON THE IMPACT PROPERTIES OF IODIDE TITANIUM

A-16316

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FIGURE 43. EFFECT OF COMBINATION OF OXYGEN AND HYDROGEN ON THE IMPACT PROPERTIES OF A TI-5Al ALLOY

A-16317

mix high-hardness (high-interstitial content) sponge with low-hardness sponge when melting alloys to meet strength specifications. An alternative method of improving the strength of alloys made with low-hardness sponge would be to add small quantities of substitutional alpha solutes. It is the purpose of this section of this report to appraise the merits of using substitutional alpha solutes.

Aluminum and tin are the two elements which can be considered for this application. Considerably more data are available on aluminum additions to titanium than on tin additions. The two elements appear to be equivalent in strengthening effects at low alloy contents. Approximately 3 per cent aluminum or tin is equivalent to 0.1 per cent oxygen in strengthening effect in iodide titanium, as shown in Figure 44. However, when added to a sponge base, the effectiveness of aluminum is considerably increased over that of tin because of the greater strengthening effect of combinations of aluminum and interstitials than of combinations of tin and interstitials (see Figure 22). The effect of aluminum and tin on the tensile properties of a sponge titanium of 55,000 psi yield strength is shown in Figure 45.

The use of interstitials to strengthen titanium and titanium alloys has the following disadvantages:

- (1) Because of the small quantity of interstitials required for a given strength increase, there is a great opportunity for ingot inhomogeneity
- (2) Toughness is sacrificed
- (3) Room-temperature strength is gained without a corresponding increase in elevated-temperature strength
- (4) Beta-decomposition reaction rates are increased
- (5) Bend ductility and formability are decreased
- (6) Weld ductility is decreased.

Aluminum and tin additions as substitutes for the interstitials overcome five of these six disadvantages. Because larger quantities are required for a given strength increase, better control of ingot homogeneity should be obtained. Toughness of substitutional alpha alloys is much better for a given strength level than of interstitial alpha alloys, as shown in Figure 46. Other ductility parameters are about the same for both types of alpha alloys. Substitutional alpha alloys maintain higher strengths at elevated temperatures than do interstitial alpha alloys as shown in Figure 47. Aluminum and tin in alpha-beta alloys are believed to slow down the beta-to-alpha reaction rates, whereas the interstitials definitely increase the rates. Like the interstitials,

FIGURE 44. EFFECT OF ALUMINUM, TIN, AND OXYGEN ON THE TENSILE PROPERTIES OF IODIDE TITANIUM

A-16318

FIGURE 45. EFFECT OF TIN AND ALUMINUM ON THE TENSILE PROPERTIES OF MAGNESIUM-REDUCED TITANIUM

A-16319

910 179
075

FIGURE 46. COMPARISON OF SUBSTITUTIONAL AND INTERSTITIAL SOLUTIONS WITH RESPECT TO COMBINATIONS OF STRENGTH AND DUCTILITY AND TOUGHNESS

FIGURE 47. THE TENSILE STRENGTH OF INTERSTITIAL AND SUBSTITUTIONAL ALPHA SOLID SOLUTIONS

From Suiter⁽⁹⁾

Alloys shown are sponge base.

A-15733

substitutional alpha solutes decrease bend ductility and formability, so they offer no advantage in this respect. Alpha alloys with tin and aluminum are ductile as welded.

It appears, therefore, that there is much to be gained by using substitutional alpha solutes to replace interstitial alpha solutes for strengthening titanium alloys. In fact, this is being done in the new alloys under development at the present time. Such alloys as Ti-6Al-4V and Ti-7Al-3Mo are utilizing the advantages of aluminum as an alpha strengthener. However, there is still considerable research to be done on the use of small quantities of alpha solutes to replace interstitials in unalloyed titanium or existing titanium alloys.

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APPENDIX A

LISTING OF GOVERNMENT RESEARCH PROJECTS
DIRECTLY RELATED TO THE EFFECTS OF
CARBON, OXYGEN, AND NITROGEN ON
TITANIUM ALLOYS

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LISTING OF GOVERNMENT RESEARCH PROJECTS
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Wright Air Development Center Contracts

Title: Precipitation Hardening and Embrittlement of High-Strength Titanium Alloys.

- Objectives:
- (a) Fundamental study of the mechanism of hardening and embrittlement associated with omega-phase formation.
 - (b) Determination of the crystal structure of the omega phase and its orientation with the alpha and beta lattices.
 - (c) Determination of the cause of hardening, i. e., whether by coherency or not.
 - (d) Study of the effect of alloy content and interstitial level.
 - (e) Detection of embrittling precipitate or interstitial concentration.
 - (f) Fundamental study of slip and deformation mechanisms in beta-embrittled alpha-beta alloys.
 - (g) Determination of effect of aluminum on beta embrittlement.

Contract: AF 33(616)-445, Supplementary Agreement No. 7. Preliminary work on Phase I in AF 33(038)-3726.

Contractor: Battelle Memorial Institute.

Status: In progress.

Title: The Gaseous Contamination of Titanium Alloys.

Contract: AF 33(600)-21277.

Contractor: General Electric Company, Evendale, Ohio, Battelle Memorial Institute.

Status: Completed, 1954.

Title: Determination of Diffusion Rates in Titanium-Base Alloys.

Objective: To determine the diffusion rates in titanium of Cr, Mn, Mo, Fe, and Al, common alloying elements in commercial titanium alloys and of H, N, C, often present in commercial alloys.

Contract: AF 33(616)-103.

Contractor: Battelle Memorial Institute.

Status: Completed, 1953.

Title: Investigation on Effects of Carbon, Oxygen, and Nitrogen on the Properties of Welds in Titanium Sheet.

Contract: AF 33(038)-21385.

Contractor: Battelle Memorial Institute.

Status: Completed, 1952.

Title: Research on the Effect of Hydrogen, Oxygen, Nitrogen, and Carbon on the Properties of Welds in Titanium.

Objective: Determination of physical properties of standard welds on titanium sheet containing controlled amounts of oxygen, hydrogen, nitrogen, and carbon in combinations.

Contract: AF 33(616)-2228.

Contractor: National Research Corporation, Cambridge, Massachusetts

Status: In progress.

Title: The Effect of Grain Size on the Mechanical Properties of Titanium and Its Alloys.

Objective: To study the effects of grain size and grain shape on the mechanical properties of an alpha alloy (unalloyed titanium), an alpha-beta alloy (Ti-2.5Mo-2.5Cr), and a beta alloy (Ti-7.5Mo-7.5Cr), and stabilization of the Ti-2.5Mo-2.5Cr alloy.

Contract: AF 33(616)-412.

Contractor: Battelle Memorial Institute.

Status: Completed, 1955.

Title: Strain-Rate Sensitivity of Titanium-Base Materials.

Objective: To determine the effects of rate of loading upon the mechanical properties of commercially available material and high-purity titanium with varying amounts of interstitials at temperatures from -180 to 800 F and strain rates from 0.006 to 60 per cent per hour.

Contract: AF 33(038)-21912.

Contractor: Rem-Cru Titanium, Inc., Midland, Pennsylvania.

Status: Completed, 1955.

Title: Development of Titanium Alloys of High Elastic Modulus.

Objective: To seek means for increasing the ratio of elastic modulus to density for titanium alloys, by varying composition and by heat treatment, providing accessory properties are not deleteriously affected.

Contract: AF 33(616)-2355.

Contractor: Armour Research Foundation.

Status: Completed, 1955.

Title: Titanium Phase Diagrams.

Objective: Determination of the Ti-Cr-Fe, Ti-Al-O, Ti-Al-N, Ti-Al-C phase diagrams over limited portions of these alloy systems. Also includes a study of the ternary oxide phases of Ti-O-Fe, Cr, Ni, Mo, and W systems.

Contract: AF 33(038)-8708 (blanket contract).

Contractor: Armour Research Foundation.

Status: Completed, 1952.

Title: Phase Diagrams of Ti-Al, Ti-Cr-Fe, and Ti-O Alloy Systems.

Contract: AF 33(038)-8708 (blanket contract).

Contractor: Armour Research Foundation.

Status: Completed, 1952.

Title: Titanium-Manganese, Titanium-Tungsten, and Titanium-Tantalum Phase Diagrams.

Objective: Determination of phase diagrams of the systems Ti-Mn, Ti-Ta, and Ti-W, using both iodide titanium and commercial-purity titanium as alloying bases.

Contract: AF 33(038)-8544.

Contractor: Battelle Memorial Institute

Status: Completed, 1953.

Title: Titanium-Rich Ti-Cr-O Ternary System.

Contract: AF 33(038)-8754.

Contractor: Massachusetts Institute of Technology.

Status: Completed, 1952.

Title: Investigations of Ternary Systems, Oxygen and Two Metals, Including Titanium.

Contract: (PR 583303).

Sponsor: U.S. Air Force, Wright Air Development Center.

Status: Contract not yet awarded.

Title: Research and Development on the Phase Diagrams of Ti-Mo, Ti-Cb, and Ti-Si Alloy Systems.

Contract: AF 33(038)-8708 (blanket contract).

Contractor: Armour Research Foundation.

Status: Completed, 1951.

Title: Development of Improved Titanium-Base Alloys.

Objective: To develop a high-strength, heat-treatable sheet alloy with good formability.

Contract: AF 33(616)-2901.

Contractor: Battelle Memorial Institute.

Status: In progress.

Title: USAF Handbook on Titanium.

Objective: To compile available information and to write a reference book on titanium. The book will be published in two parts. The first part was printed in August, 1954, and distributed in February, 1955, and covers the production of titanium and titanium alloys, the physical metallurgy of titanium, and the properties of titanium and titanium alloys. The second part will contain information on laboratory procedures and fabrication of titanium and titanium alloys.

Contract: AF 33(616)-2222.

Contractor: H. K. Adenstedt.

Status: In progress.

Army Ordnance Contracts

Title: Development of Transformation Data for Special Titanium Alloys.

Contract: DA-11-022-ORD-1292.

Contractor: Armour Research Foundation.

Status: Completed, 1955.

Title: Free Energy of Oxygen in Titanium Metal.

Objective: Study of partial free energy of oxygen in the titanium-oxygen solutions up to 1 per cent by weight and at temperatures up to 2500 C.

Contract: NoWR 1424 (00).

Contractor: Arthur D. Little, Inc., Western Laboratory Division, San Francisco, California.

Status: Completed.

Title: Creep-Rupture Characteristics of Titanium and Its Alloys.

Objective: Testing of Ti-0.35 O and Ti-Si-Al alloys carried out at 1000, 1200, 1400, and 1600 F.

Contract: DA-19-020-ORD-2787.

Contractor: Massachusetts Institute of Technology, Cambridge, Massachusetts.

Status: Completed, 1954.

Title: The Development of Strong, Tough Titanium Alloys.

Objective: Determination of the effects of C, O, and N on strength and toughness properties.

Contract: DA-19-059-ORD-123 (continued as DA-19-059-ORD-1007).

Contractor: Rem-Cru Titanium, Inc., Midland, Pennsylvania.

Status: Completed, 1952.

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Title: Continued Research and Development for Development of Strong, Tough, Titanium Alloys.

Objective: Study of the effect of nitrogen on physical properties and toughness when added to Ti-7Mn and Ti-5Al-2.5Sn alloys. Study of heat treatment of alpha-beta alloy (Ti-7Mn); and supply sheet for further testing.

Contract: DA-19-059-ORD-1007 (continuation of DA-19-059-ORD-123).

Contractor: Rem-Cru Titanium, Inc., Midland, Pennsylvania.

Status: Completed, 1953.

Title: Transformation Kinetics in Commercial Alloys and Their Iodide Purity Analogues.

Objective: Study of effect of cooling rate on microstructure and hardness of Ti-150A, RC-130A, and RC-130B.

Contract: DA-04-495-ORD-18 (blanket contract).

Contractor: California Institute of Technology, Jet Propulsion Laboratory, Pasadena, California.

Status: In progress.

Title: Solid-Solution Hardening of Alpha and Beta Titanium.

Objective: A study of binary additions of Al, Fe, B, Mo, Cr, Si, O, N, and C to iodide titanium.

Contract: DA-11-022-ORD-1439.

Contractor: Armour Research Foundation.

Status: Completed, 1955.

Title: Binary Alloys of Titanium with Carbon, Nitrogen, Oxygen, and Boron.

Contract: DA-30-069-ORD-76 (extended to DA-30-069-ORD-935).

Contractor: New York University.

Status: Completed, 1952.

Title: Research and Development on Titanium-Aluminum-Oxygen System.

Objective: Determine isothermal sections at 850 and 1000 C for alloys up to 10 per cent aluminum and vertical sections at 0.1 and 0.3 per cent oxygen from 700 to 1300 C, carrying out age-hardening studies on 10 per cent aluminum alloy.

Contract: DA-30-069-ORD-4181.

Contractor: New York University.

Status: In progress.

Title: The Research of Ti-Rich Ternary Diagrams with the Alloying of C-O and C-N.

Objective: Phase-diagram study of Ti-O-N, Ti-Mn-Fe, Ti-Mn-O, Ti-Mo-Al, Ti-Fe-Mo, Ti-Mo-O, and Ti-Pb.

Contract: DA-30-069-ORD-208 (continued as DA-30-069-ORD-1284).

Contractor: New York University.

Status: Completed, 1953.

Title: Effect of Purity, Microstructure, and Cold Work on Fatigue Behavior.

Objective: To study effect of C, N, and O, cold work, and temperature on fatigue behavior of Ti and Ti alloys.

Contract: DA-30-069-ORD-213.

Contractor: Kennecott Copper Corporation, New York.

Status: Completed, 1952.

Title: Research and Development on Characteristics of H, O, and N in Ti.

Objective: Determine quantitatively the influence of O, N, and H on kinetics of the isothermal transformation and martensite reaction in the systems Ti-Mn, Ti-Cr, and Ti-Al. Determine effect on microstructure, hardness, and tensile properties of the composition of the alloys (i. e., percentage of H, N, and O).

Contract: DA-30-069-ORD-644.

Contractor: Columbia University, New York, New York.

Status: Completed, 1954.

Title: Grain-Size Control.

Objective: Determine effect of 50 alloying elements on beta grain size.

Contract: DA-30-069-ORD-840 (Part II).

Contractor: New York University.

Status: Completed, 1953.

Title: Research Study of Impurities and Manufacturing Variables of Titanium Alloys.

Objective: To study the effects of hydrogen on the mechanical and metallurgical properties of Fe-Cr, Fe-Mo (Ti-140 type), 5-Al, Fe-Cr, and Fe-Mo (Ti-155AX type).

Contract: DA-30-069-ORD-1157 (continuation of DA-30-115-ORD-7).

Contractor: Titanium Metals Corporation of America.

Status: Completed, 1955.

Title: Titanium Phase-Diagram Study.

Objectives: Determine (a) The titanium-rich end of the Ti-Cr-V phase diagram up to 40 per cent V and 40 per cent Cr over the temperature range to the solidus.
(b) The titanium-rich end of the Ti-Si-C diagram to 25 per cent Si and 5 per cent C.
(c) The titanium-rich end of the Ti-N-H diagram to 8 per cent N and up to and including the homogeneity region of the delta phase of the Ti-H system up to 1000 C.

Contract: DA-30-069-ORD-1216.

Contractor: New York University.

Status: Completed, 1954.

Title: The Yield Point in Polycrystalline Titanium.

Objective: To determine the effect of controlled amounts of interstitial and of substitutional alloy elements upon the temperature range in which the yield point and other strain-aging effects occur in iodide titanium. Study the validity of Cottrell dislocation needed for the yield point and calculate the activation energy involved.

Contract: DA-30-069-ORD-1217.

Contractor: New York University.

Status: Completed, 1954.

Title: Influence of Oxygen, Hydrogen, and Nitrogen on the Transformation Characteristics in Some Titanium Alloys.

Contract: Continuation of DA-30-069-ORD-644.

Contractor: Columbia University, New York, New York.

Status: Completed, 1954.

Title: Research and Development on the Influence of Oxygen on the Transformation Characteristics of Some Titanium-Molybdenum Alloys.

Contract: DA-30-069-ORD-1420.

Contractor: Columbia University, New York.

Status: Completed, 1955.

Title: High-Strength, High-Toughness Alloys for Ordnance Applications.

Contract: DA-30-115-ORD-7.

Contractor: Allegheny Ludlum Steel Corporation.

Status: Completed, 1953.

Title: Microstructures and Their Effect on Commercial-Purity Substitutional Alloys.

Objective: Comparison of mechanical properties of specimens heat treated to the same hardness by (1) isothermal decomposition and (2) quenching and reheating for isothermal precipitation hardening.

Contract: DA-33-019-ORD-206.

Contractor: Case Institute of Technology, Cleveland, Ohio.

Status: Completed, 1952.

Title: Surface Hardening of Titanium by Carburizing and Induction Heat.

Contract: DA-33-019-ORD-216 (continued as DA-33-019-ORD-942).

Contractor: Battelle Memorial Institute.

Status: Completed, 1952.

Title: Small Titanium Castings.

Objective: Development of mold materials for shaped castings. Project aimed at developing molds that would give good surfaces on the castings and avoid surface contamination.

Contract: DA-33-019-ORD-223.

Contractor: Battelle Memorial Institute.

Status: Completed, 1954.

Title: Effect of Microstructure on Properties of Titanium Alloys Made with Iodide Titanium.

Objective: Title sufficiently descriptive.

Contract: DA-33-019-ORD-280 (continued as DA-33-019-ORD-1397).

Contractor: Battelle Memorial Institute.

Status: Completed, 1953.

Title: Effects of Interstitial Elements on Welds in Alpha-Beta Titanium Alloys.

Contract: DA-33-019-ORD-1524.
Contractor: Battelle Memorial Institute.
Status: Completed, 1955.

Title: Research and Development to Determine Rate of Diffusion of Carbon in Alpha and Beta Ti as a Function of the Temperature and Concentration.

Contract: DA-36-034-ORD-1157.
Contractor: Horizons, Inc.
Status: Completed, 1954.

Title: The Effect of C, N, O, and B on the Structure and Properties of Titanium.

Objective: Study of the effect of interstitials on impact properties.
Contract: Project TB 4-15.
Contractor: Watertown Arsenal Laboratory.
Status: Completed, 1954.

Title: Surface Embrittlement of Titanium by Exposure of Weld Heat-Affected Zone to Atmosphere.

Objective: Investigation of the extent of penetration of polycomponent systems of oxygen, nitrogen, and hydrogen into the surface of titanium at the elevated temperatures and short times associated with welding, and to evaluate the effect of such surface contamination on notch toughness and ductility in titanium weldments.
Contract: Project TB 4-31.
Contractor: Watertown Arsenal Laboratory, Internal Project.
Status: Completed, 1954.

Title: Effect of Atmospheric Contaminants on Properties of Titanium Welds.

Objective: To determine quantitatively the effect of contaminants on the fatigue properties, corrosion resistance, and ductility of titanium weld deposits on unalloyed and alloyed sheets of 0.10-, 0.25-, and 0.50-in. thicknesses.
Contract: Project TB 4-31.
Contractor: Bureau of Mines, College Park, Maryland, Physical Metallurgy Branch.
Status: Completed, 1955.

Title: Determination of the Notch Sensitivity of Weld Heat-Affected Zones
in Various Alloys.

Objective: Investigation of the Charpy notch impact properties of weld
heat-affected zones by a "synthetic specimen" technique.

Contract: DA-30-115-ORD-490.

Contractor: Rensselaer Polytechnic Institute, Troy, New York.

Status: Completed, 1954.

U. S. Navy Contracts

Title: Determination of Ti-O Phase Diagram.

Contract:

Contractor: Naval Research Laboratory.

Status: Completed.

Title: Mechanism of Oxidation of Titanium.

Contract: N6onr04704.

Contractor: Carnegie Institute of Technology.

Status: Completed, 1952.

Title: Free Energy of Dilution of Oxygen-Titanium Alloys.

Contract: Nonr 1587 (00).

Contractor: Chicago Development Corporation, Riverdale, Maryland.

Status: Completed, 1955.

Title: Titanium Armor Plate.

Objective: To make systematic additions of interstitials of carbon, oxygen, nitrogen, and hydrogen to determine effects on ballistic performance.

Contract: NOrd 12515.

Contractor: Rem-Cru Titanium, Inc., Midland, Pennsylvania.

Status: Completed, 1955.

Title: Titanium Alloy Plates.

Objective: To produce all-alpha titanium alloys for ballistic testings by WRL and NPG of composition Ti-5, 10, and 15Sn and Ti-3 and 6Al, Ti-5Al-5Sn and Ti-3Al-10Sn, and interstitial contents as determined under NOrd 12515.

Contract: NOrd 15002.

Contractor: Rem-Cru Titanium, Inc., Midland, Pennsylvania.

Status: In progress.

Title: Armor, Nonferrous.

Objective: To try out titanium-armor fabrication methods for eventual adoption by industry.

Contract: Allotment 45404 (FY 55).

Contractor: Naval Gun Factory, Washington, D. C.

Status: In progress.

Title: Titanium Hard-Faced Armor.

Objective: Development of face-hardened compacted titanium for armor.

Contract: NOrd-13777.

Contractor: Brush Development Company, Cleveland, Ohio.

Status: Completed, 1955.

Title: Investigation of Nitriding of Titanium by Heating in Air with Reducing-Atmosphere Flame Torch.

Contract: NS 622-060.

Contractor: U. S. Navy, Engineering Experiment Station, Annapolis, Maryland.

Status: Completed, 1953.

Title: Deoxidation of Molten Titanium with Selected Reducing Agents.

Contract: P. O. 23794.

Contractor: Naval Research Laboratory, Washington, D. C.

Status: Completed, 1955.

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APPENDIX B

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APPENDIX C

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NOTE TO RECIPIENTS OF TML TECHNICAL REPORTS

The list below describes all reports that have been prepared thus far by the Titanium Metallurgical Laboratory. It includes nontechnical progress statements to the Defense Department Steering Group on Titanium Research and Development, the agency which has technical cognizance over the Titanium Metallurgical Laboratory. It also includes several special reports prepared specifically for the Steering Group. The reports which have been approved for general distribution are starred below. TML Report No. 8 has been given only limited distribution because the same material has now been published in Iron Age magazine. TML Report No. 10 is ready for general distribution as soon as approval to publish it is received.

<u>Report Number</u>	<u>Title</u>
1	Summary Report on Visits to West Coast Aircraft Manufacturers
1A	Visits of Steering Group to Aircraft Manufacturers
2	First Progress Statement to Steering Group, February, 1955
3	Second Progress Statement to Steering Group, March, 1955
4	Notes on the Fabrication and Use of Titanium (To the Materials Advisory Board of the National Academy of Science)
5	The Use of Titanium Alloy Sheet in Airframe Components
*5A	The Use of Titanium Alloy Sheet in Airframe Components (TML No. 5 revised)
6	Third Progress Statement to Steering Group, April, 1955
*7	Survey of the Problem of Delayed Cracking in Formed Titanium Parts
8	Principles and Practical Aspects of Titanium Heat Treatment [not given general distribution because it was published in <u>Iron Age</u> (June 30, 1955)]
9	Fourth Progress Statement to Steering Group, May, 1955
10	A Study of the Air Contamination of Three Titanium Alloys
11	Report to the Steering Group on Titanium Fasteners
*12	Formability Tests on Titanium Alloy Sheet
*13	Selection of Materials for High-Temperature Applications in Airframes
14	Fifth Progress Statement to Steering Group, June, 1955
*15	Engineering Properties of Commercial Titanium Alloys (To be issued in October)
16	Recommendation for Augmented Research and Development on Titanium
17	Sixth Progress Statement to Steering Group, July, 1955
*18	Analysis and Laboratory Examination of Aircraft Parts Which Failed by Delayed Cracking
*19	General Summary of the Physical Metallurgy of Titanium Alloys
*20	Effect of Carbon, Oxygen, and Nitrogen on the Mechanical Properties of Titanium and Titanium Alloys

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