FIRST PROGRESS REPORT

ON

A STUDY OF CREEP OF TITANIUM AND TWO OF ITS ALLOYS

January 1, 1951

AIR FORCE CONTRACT NUMBER: AF33(618)-1111
EXPENDITURE ORDER NUMBER: 480-36 BR-1
SUMMARY

The objective of the investigation is to explain in terms of fundamental concepts how metallurgical variables affect the creep of titanium in the atmospheric temperature range. The variables to be investigated include composition, heat treatment and cold work. The contract specifies that the work be carried out on commercially available sheet of titanium and two titanium alloys. These will represent the range of compositions to be studied. Heat treatments and cold work will be systematically varied insofar as possible and related to the observed creep behavior. Microstructural examination and X-ray diffraction analysis will be the major tools used to obtain the objective of the investigation.

The problem arose from fragmentary data which indicates that titanium will creep at room temperature under stresses well below the yield strength. Consequently the major interest is in the creep of the test materials at or slightly above room temperature. The contract specifies that the work be carried out in the range from -100° to 600° F, on the basis that sheet titanium might be expected to encounter temperatures in this range or that the fundamental explanation may require testing in this range.

The work covered to date has almost entirely been confined to preparation of equipment and development of the application of the necessary experimental techniques to the analysis of the creep of titanium. The major reason for this is that the producing companies have been unable to supply the test stock. An order was placed with the Remington Arms Company in July 1950 for a supply of their 130A alloy. The commercial titanium sheet 75A and an alloy 150A were ordered from the Titanium Metals Corporation in September 1950. Using the most realistic delivery dates then available, it seemed as if at least one
of the test materials ought to have been available by November 1950. No deliveries have been made and at the time this is written a reliable future date of delivery cannot be obtained.

Equipment has been set up to operate at 72° F, -30°F, -100°F, and from 200° to 600° F. Experimental work, largely of a technique development and theory checking type is in progress on a small amount of titanium sheet of uncertain composition donated to the investigation.

The report outlines the proposed program and the reasons for the approach being used insofar as is possible until experimental results are obtained to act as a guide.
INTRODUCTION

The objective of this investigation is to study the creep of titanium so as to lead to some explanation of the factors affecting the creep behavior of commercial titanium and titanium alloys within the atmospheric temperature range. The Air Force directed that the work be carried out on sheet of commercially pure titanium and two commercially available alloys; and that the effect of such metallurgical variables as cold rolling and heat treatment should be investigated. Explanation of creep behavior in terms of such internal structural conditions as strain and precipitation reactions are expected.

The problem arose from the concern caused by the observation of excessive creep of commercially pure titanium at room temperature under stresses well below the yield strength. The experimental investigation will therefore be primarily concerned with the metallurgical variables affecting creep of titanium at room temperature. The phenomena will, however, be investigated if necessary at temperatures ranging from -100° F to as high as 600° F.

Commercially available materials were specified for the investigation in order to have results which could be directly applied to the practical use of such materials. Rolled sheet stock was dictated in view of the ultimate use of most concern. While creep tests are to be made under practical engineering conditions, it is not the purpose of the investigation to provide engineering design data. Instead it is planned to define the factors controlling the low temperature creep of titanium in terms of fundamental parameters.

Due to the inability of commercial companies to deliver suitable test material, this present report does not present data bearing directly on the
problem. The plan of the investigation is outlined and the considerable amount of work which has been done to prepare suitable test equipment and to develop techniques is described. A small amount of test data have been obtained on sheet stock of uncertain composition which was donated to the investigation.

**TEST MATERIAL**

Three grades of 0.060-inch sheet were ordered for the investigation, after consultation between representatives of the Office of Air Research and the University, as follows:

Nominal Chemical Composition (percent)

<table>
<thead>
<tr>
<th>Trade Designation</th>
<th>O2</th>
<th>N2</th>
<th>C</th>
<th>Fe</th>
<th>Cr</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>75a Commercially pure Ti</td>
<td>trace</td>
<td>0.02</td>
<td>-</td>
<td>0.10</td>
<td>-</td>
<td>Titanium Metals Corp.</td>
</tr>
<tr>
<td>130A</td>
<td>Mn principal alloying addition</td>
<td>0.25</td>
<td>.02</td>
<td>.02</td>
<td>1.3</td>
<td>2.7</td>
</tr>
<tr>
<td>150A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Titanium Metals Corp.</td>
</tr>
</tbody>
</table>

The 75A and 150A material was ordered for delivery to the University by the Air Materiel Command under Purchase Order Number (33-038)51-1257 dated 28 September 1950 to the following specifications:

75A - commercially pure titanium sheet - low carbon - high ductility - maximum longitudinal yield strength for 0.2-percent offset 60,000 psi - annealed - 15 square feet, 0.06-inch thick by 12-inch width minimum.

150A - titanium alloy sheet - annealed - 12 square feet, 0.06-inch thick by 12-inches width minimum.

Twelve square feet of 0.06-inch sheet of the 130A material was ordered from the Rem-Cru Corporation in July 1950 by the University, with the approval of representatives of the Office of Air Research, in order to
attempt to hasten delivery of test stock and reduce delay in initiating the investigation.

At the time this report was written it has not been possible to obtain delivery of any of the three items in spite of urgent following of the orders by the University through all possible contacts with the producers. The reasons given for the delays in delivery have been manufacturing difficulties. The latest word has indicated that rolling difficulties will require holding up the orders until procedures are so standardized as to be able to provide a material representative of future commercial production.

A small amount of "commercially pure" titanium has been given to the investigation for starting the work. It was in the form of strips approximately 0.09-inch thick by 2-inch wide. No analysis of the material was supplied. Metallographic examinations of the material indicate the presence of considerable contamination.

PROCEDURE

The investigation includes planning the experimental procedures; procurement and erection of the special creep testing equipment; development of the application of techniques, widely used by the University on other materials for the same objectives, to the special case of titanium; and finally the actual experimental investigations.

In general, a program is required in which the effect of conditions of heat treatment, cold work, and composition on the creep resistance of titanium is evaluated by testing. Fundamental explanations of the results are then to be established using modern theory of creep.

The following general procedure is planned, although this should be recognized as being flexible to the extent that it will be modified as is dictated by data as it is obtained:
Creep Testing

All materials will be initially tested at room temperature. Each material will be subjected to stresses above and below the yield strength. Those materials subject to appreciable creep at room temperature will be tested at -30° F in a cold room. Again those which creep to an appreciable extent at -30° F will be tested at -100° F.

Those materials which do no creep at room temperature will be tested first at about 200° F and if necessary at temperatures up to 600° F. In addition tests will be made at temperatures above room temperature as necessary to aid in clarifying fundamental factors.

It is intended to use room temperature for the main sorting temperature insofar as possible. This should work well for the commercial titanium. Higher temperatures may, however, be necessary for the alloy materials.

Fundamental Studies

On the basis of considerable experience in this field the program planned may be summarized as follows:

1. Correlate the observed creep behavior with metallurgical variables. These will include chemical composition, heat treatment in the case of the alloys and cold work in the case of the commercially pure material. Insofar as possible the results will be systemized. Due to the limited compositions to be studied it is anticipated that only qualitative trends at best will be obtained for composition. Heat treatments and cold work ought to give more consistent results in that the conditions can be varied systematically.

Because titanium and its alloys are subject to phase changes on cooling from heat treating above limiting temperatures, types and
conditions of prior heat treatment ought to be influential on creep characteristics. It is expected that it will be necessary to vary heat treating temperatures, cooling rates, and subsequent subcritical heat treatments systematically to obtain an insight into the relationship between prior treatment and creep characteristics.

Care will be taken to insure that such phenomena as precipitation and other aging effects are clarified. Because the amount of test material is limited, it is not planned to carry out extensive ordinary physical testing to follow such effects. Hardness tests will be made and such tensile or bend tests as may be useful before and after creep testing.

Cold work will be carried out for varying reductions on the commercially pure material over such ranges as may be necessary to define its effects on creep properties. Initial heat treatment within practical limits may be varied although it is planned to use the commercial annealed condition as a base treatment. Annealing after cold work will be used to clarify the mechanism of improvement or deterioration of creep resistance by cold work.

2. Experience has proven that microstructural studies and hardness measurements are very imperfect indicators of the fundamental causes for variation in creep resistance with composition or prior treatment. As far as is now known the structural conditions which control creep resistance are on a much smaller scale than can be measured by such methods. For this reason major reliance for explanation of the creep behavior must be placed on X-ray diffraction characteristics.

A present theory of the creep phenomena is largely based on periodicity of internal strains and activation energy as they
affect the generation and movement of the dislocations by which creep is assumed to occur. The best tool now available for the study of these phenomena is broadening of X-ray diffraction lines. The sharpness of such lines is believed to be a function of local internal strains within the lattice of the matrix which have a periodicity of the right magnitude to effect the small scale deformations by which creep is believed to occur. For this reason line broadening measurements will be the most fundamental measurements of the investigation.

Since cold work is also both a large and small scale strain phenomena, the only reliable method therefore of measuring its effect is by line broadening studies. Hardness measurements cannot be solely relied upon to properly measure this effect for fundamental explanations.

Because the fundamentals of creep are so dependent on internal strain phenomena, it is expected that relaxation characteristics are closely allied to creep resistance. For instance, maintenance of improvement in creep resistance from strains induced by cold work should continue up to the temperature at which relaxation of such strains will occur. Consequently simple stress-relief experiments followed by line-broadness determinations should predict the temperature and time conditions over which creep improvement from these sources will be maintained. Likewise the theory can be checked by determining whether the creep resistance remains constant at a given internal strain regardless of whether this strain is obtained by direct cold work or by excess cold work followed by stress relief.

The fundamentals of the influence of the type of transformation
products on creep resistance are not as well understood. It is expected, however, that they will again be a function of internal strain and the relaxation characteristics. It is therefore proposed to use that approach as a first step in the analysis of such effects.

Precipitates with a distribution and size suitable for improving creep strength are generally too small to be resolved by the light microscope. Greater resolution can be obtained from the electron microscope and it will be used to obtain information about the character and spacing of such precipitates if found. It may be necessary to use special heat treatments to develop the precipitates to a size which can be resolved even by the electron microscope. The same technique will be used if grain boundary phenomena are suspected of contributing to the creep behavior.

Prior Treatment Details

The inability to obtain delivery of test stock has considerably hampered the development of a detailed experimental program. For the present it is planned to use the donated stock principally to outline the effects of cold rolling. For this purpose a program is underway to establish the conditions of reheating which will cause recovery of this stock, as measured by X-ray diffraction line sharpening after 100-percent reduction at room temperature. Samples are being heated for time periods up to 1000 hours at 400, 500, 700, 800 and 900°F and the recovery characteristics measured. Simultaneously samples with reductions of 5, 15 and 20 percent are being prepared and will be creep tested at room temperature. Additional creep testing will be made at higher temperatures to determine the relation between recovery characteristics and maintenance of increased creep resistance from cold work. In addition
tests will be made on specimens partially recovered before creep testing to determine if the same creep strength internal strain relationship holds as for unrecovered materials.

Until the results of this work are obtained a detailed plan for work on the 75A material will not be made.

Some preliminary work will be necessary on the heat treating and cold working characteristics of the 130A and 150A materials before detailed programs can be outlined for these materials.

Results

Most effort has been expended on the erection of equipment and development of techniques. A small amount of data has been accumulated for the impure titanium sheet donated for the investigation.

Equipment

1. Ten existing creep units of a simple lever type have been moved to, and set up in, a constant temperature room. The room is adjacent to a laboratory which is maintained at 72° + 1° F for other work. It was necessary to extend the air conditioning equipment to the available space and to increase the capacity of the air conditioning unit to the extent of installing additional compressor capacity.

This equipment is complete and has been operated.

2. Plans are to move five of the units from the room at 72° F to a cold room which can be held as low as -30° F where it is necessary to run tests at lower temperatures.

3. A single station unit has been adapted to operate at -100° F. The
specimen will be cooled to this temperature in air cooled in turn by suitable liquids.

4. A five station unit built to operate with a recirculating air atmosphere is nearly completed for the tests at temperatures between 70° F and 600° F.

5. Occasional tests which may be needed for the higher temperatures when the recirculating furnace is operating at another temperature than that needed, can be made in the standard creep units available at the University.

Technique Development

A considerable amount of effort has been expended on methods of measuring creep, heat treatment of titanium, metallographic procedures and X-ray diffraction methods.

Creep Measurements

For all tests up to 212° F it is planned to use SR-4 strain gauges to measure creep. Specimens will be made with three different gauge sections so that creep characteristics for three different stresses will be obtained from each test. For tests at higher temperatures it will be necessary to use other means of measuring extension. The modified Marten's optical type extensometer used for other creep testing work at the University has been adapted to the sheet specimens. It will not be possible to obtain curves for more than one stress per test with this latter system.

Due to the low modulus of titanium and the large amount of first-stage creep it will be necessary to use gauges capable of measuring greater extension than the usual SR-4 gauges. "Post-yield" gauges capable of measuring extensions up to 10-percent with the same sensitivity have been obtained from
Ruge-DeForest Company. The strain indicator has been modified to the wider range.

Heat Treatment

Protection from oxygen and nitrogen will be necessary for all heat treatments at high temperatures. The stock being tested is thin sheet for which it will not be possible to remove altered surface layers. A muffle furnace utilizing an argon atmosphere has been prepared for this purpose.

Preliminary heat-treatment studies on the stock now available indicated that surface attack occurred to a depth of 0.004-inch when samples were annealed in air at 1600° F. This can be tolerated for preliminary work; but will not be satisfactory for the commercial material being obtained for the main program. Consequently all future treatments at high temperatures will be carried out in the argon atmosphere.

For prolonged aging and recovery treatments at temperatures below 1200° F which may require protection from the atmosphere, the specimens will be sealed in pyrex tubes under vacuum. Preliminary results indicate that this will not be necessary up to 900° F, at least for samples which will only be subjected to metallographic examination. No increase in the depth of surface alteration could be detected, in samples originally annealed at 1600° F and cold worked, after holding in air at 900° F for recovery.

Cold Working

Small samples suitable for metallographic and x-ray studies can be rolled in a mill, available at the University. The longer samples needed for creep testing cannot be rolled in this mill because it is not built for or equipped to produce flat strips of any length.

Arrangements have been made to have rolling of stock for creep tests done by the Hoskins Manufacturing Company in Detroit, Michigan.
Metallographic Examination

The methods of preparing titanium for metallographic examination presented in the Titanium Symposium and in Industrial and Engineering Chemistry for February 1950 have been utilized successfully. Methods of electrolytic polishing have been investigated without much success although further attempts to adapt these methods are being continued.

Samples of 150A alloy bar stock from another investigation in progress at the University have been obtained and are being used to develop familiarity with the microstructure of this alloy.

X-ray Diffraction

Samples used for X-ray diffraction line analyses must have surfaces free from artificial structural alteration. An electrolytic method of surface metal removal utilizing an electrolyte of glycerine, nitric acid and hydrofluoric acids in the proportions of 3:1:1 at a current density of approximately 4.5 amperes per square inch was found to produce a surface free from disturbed metal. This method also removed the 0.001-inch surface layer attacked by air during annealing. Diffraction patterns showed that a total of 0.012 to 0.015-inch of surface had to be removed before freedom from surface alteration was attained. A water bath utilizing ordinary cold water was found to give sufficient temperature control in order to complete the etching process in about 15 minutes.

Thus far the only diffraction technique used has been the measurement line broadness for study of internal strain. The greatest sensitivity is attained for high angle diffraction lines, the (300) at 20 = 11° F for copper radiation being the best. Measurements are made with a North American Phillips high angle X-ray spectrometer with the Geiger tube connected to an automatic recorder.
Unstrained material gives a characteristic $\alpha_1 \alpha_2$ doublet shape to the diffraction line. This shape is due to so-called "instrument" broadening. Straining the metal, as in cold working, results in a merging of the doublets and a great increase in the overall line width. The quantity which must be measured is the broadening due to strain alone. The problem is to "subtract" the instrument broadening from the total broadening to obtain that due to internal strain. The result is a quantitative measure of internal strain commonly called a "smear" function.

The separation of the two components of the diffraction line is accomplished by using Fourier series to synthesize the shape of the diffraction line both for the uncold-worked and cold-worked conditions. Then a process known as "unfolding" is used to perform the separation. The actual mechanics is very tedious and will not be discussed in detail at this time. Up to the present a graphical method utilizing transparent ruled grids placed over the automatically recorded plot of the line has been used to obtain Fourier coefficients. The results indicate that the ten harmonics which can be included in the analysis by this method are insufficient. However, the use of a mechanical harmonic analyzer in the Mathematics Department of the University has been obtained. This will not only permit the use of a sufficient number of harmonics but will speed up the process.

No work has been done on techniques for measuring lattice parameters, identification of phases, or other $\lambda$-ray diffraction techniques. Known procedures should, however, be readily adaptable if and when the need for such information arises.

Experimental Data

All experimental data to date has been obtained from the apparently impure "commercial purity" stock donated for the program. This material was in the rolled condition. Small samples were heated in air for one hour and
both furnace cooled and water quenched at temperatures from 1200° to 1700° F. Both the hardness values, summarized below and X-ray diffraction patterns indicated that the best anneal (strain-free condition) was obtained by furnace cooling from 1600° F.

<table>
<thead>
<tr>
<th>Annealing Temperature (°F)</th>
<th>Hardness (Rockwell &quot;F&quot;)</th>
<th>Furnace Cooled</th>
<th>Water Quenched</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received hardness = 20.1</td>
<td>17.5</td>
<td>17.5</td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>17.5</td>
<td>17.5</td>
<td></td>
</tr>
<tr>
<td>1400</td>
<td>15.3</td>
<td>15.9</td>
<td></td>
</tr>
<tr>
<td>1500</td>
<td>14.8</td>
<td>15.9</td>
<td></td>
</tr>
<tr>
<td>1600</td>
<td>14.7</td>
<td>17.6</td>
<td></td>
</tr>
<tr>
<td>1700</td>
<td>14.8</td>
<td>18.6</td>
<td></td>
</tr>
</tbody>
</table>

Creep tests were made at room temperature (72° F) on samples annealed from 1600° F under stresses of 30,000 and 50,000 psi. No creep was detectable under the 30,000 psi stress. The 50,000 psi specimen reached second-stage creep in a short time and has continued at a rate of 1.53 x 10^-7 inch per inch per hour for over 1000 hours.

The determination of the conditions for recovery from cold work as measured by sharpening of the (300) diffraction line on reheating is partially completed. Samples annealed at 1600° F and then reduced in thickness 40 percent by rolling have been reheated for time periods up to 1000 hours at 400° and 500° F and up to 100 hours at 700° and 800° F. Longer heating time periods are in progress at the latter two temperatures, and the temperature range is being extended to 900° F. The results to date are summarized as follows:

1. No recovery could be detected in 1000 hours at 400° and 500° F.
2. Recovery does occur at 700° and 800° F.
3. The diffraction lines of samples heated for 1, 10 and 100 hours
at 700° F have been analyzed by the graphical Fourier method. Although the results are incomplete, due to the limitation of number of harmonics by this method, the indications are that extending the number of harmonics with the mechanical analyzer will yield an exact measure of recovery in terms of line sharpening.

1. Recovery is not complete in 100 hours at 800° F. An approximate evaluation of the smear function for the sample heated 100 hours indicates that 50-percent recovery was being approached. The separation of the doublet was just beginning to occur.

FUTURE WORK

Work will be continued on the material now on hand to obtain experience as a guide in evaluating the commercial test stocks when they are received. The program planned for the stock now available is:

1. Complete the recovery studies including Fourier analysis of the diffraction lines after 60-percent cold reduction out to 1000 hours at 700°, 800° and 900° F so that the recovery can be expressed quantitatively as a function of time and temperature.

2. Conduct creep tests at room temperature on annealed and cold rolled samples after reduction of 5, 15 and 60-percent at room temperature. The samples have been prepared and are at the Hoskins Company for rolling.

3. Complete metallographic examination and take photomicrographs of the stock after the various treatments.

Completion of this work should yield a sound background for outlining an experimental program when the 75A, 130A and 150A materials are received. The data will show the relationship between internal strain from cold work,
as measured by diffraction line broadening, and creep resistance at room temperature. The ranges in reduction necessary to test for fundamental explanations will be outlined.

The absence of any indication of recovery for temperatures as high as 500°F and time periods up to 1000 hours suggests that strengthening from cold work should be maintained up to these temperatures. It is planned to check this by conducting creep tests at these temperatures.

In order to obtain a better insight into the fundamentals of the creep behavior samples will be heated to allow recovery to occur to various stages. Creep tests will then be made to determine if the creep resistance is the same at a given line broadness obtained by direct rolling and by more severe rolling followed by recovery to the same line broadness. Any differences would require modifications concepts by which cold work is being measured; or in the mechanism by which cold work affects creep.

The complete program on cold rolling effects will involve evaluation of recovery in terms of percent reduction. This work will, however, be deferred until the 75A stock is received and the data from the previous program is obtained.