CANADA

THE DESIGN OF HEAT-TREATABLE TITANIUM ALLOYS

by

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ABSTRACT

Work in progress designed to arrive at a logical method for designing titanium alloys specifically for use in the heat-treated condition is described. A partial 900°C isothermal section of the titanium-aluminum-molybdenum constitutional diagram, including ternary tie-lines, has been developed and a system for the design of heat-treatable alloys based on this isothermal section is being examined. Using the criterion of tensile properties, this system involves the choice of the best β composition available on solution treatment at 900°C and the addition to it of controlled amounts of α of a fixed composition using the tie-lines as a guide. The presence of a three-phase field ($\alpha_1 + \alpha_2 + \beta$) in the system has been indicated by the tie-line directions.

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TABLE OF CONTENTS

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ILLUSTRATIONS

TABULATIONS

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INTRODUCTION

Until recently no titanium alloys have been designed specifically for use in the heat-treated condition. Commercially available alloys which are capable of being strengthened by solution treatment and ageing (the $\alpha + \beta$ alloys) were designed primarily for use in the stress-relief annealed condition and it was only after their composition limits had been defined that their optimum heat treatment was established and in some cases recommended for use. If a family of sound heat-treatable titanium alloys is to be developed, it is essential that a logical method for arriving at the optimum composition in any promising alloy system should be available.

One of the greatest handicaps to the designing of such a family of alloys is the incomplete state of nearly all published ternary diagrams involving titanium. Unlike a binary diagram a ternary, as normally published, does not give the composition and proportion of the phases present in a two-phase field. If it can be considered that the properties of a two-phase alloy are improved during heat treatment almost wholly by what happens to the β-phase, then it can be said that the basic factors to be controlled in the alloy are the composition and proportion of the β-phase. Without a means of determining and controlling these factors, the systematic design of two-phase heat-treatable alloys is necessarily difficult. The features that would provide the means of determining and controlling these factors are the ternary tie-lines.

In the present work, a design system based on the titanium-aluminum-molybdenum ternary constitutional diagram, to which tie-lines have been added, is being investigated. The following basic assumptions and considerations, which at the present time seem reasonable, have been made:

1. The heat-treatable alloy will be of the $\alpha + \beta$ type.

2. In an $\alpha + \beta$ alloy, the β should be the continuous phase since the strengthening of these alloys takes place through the precipitation hardening of the β.

3. Since the β is the most important phase, the control of the β composition and the choice of the best β are of paramount importance.

4. The best method for determining and controlling the β composition is through the re-determination of the constitution diagram of this alloy system, and the determination of the ternary tie-lines in the two-phase fields.

The criteria which might be used for judging the relative merits of the alloys produced in this investigation are many and varied, and in practice would depend upon the application for which a heat-treatable alloy was sought. However, since the aim of the present work is merely illustrative, the criteria to be used are simple room temperature tensile properties.

The above considerations and assumptions have led to the following steps or projected steps in the present research:

1. Re-determination of the titanium-rich corner of the titanium-aluminum-molybdenum system.

2. The choice of two or three reasonable solution treatment temperatures for alloys in this system. For the first series of experiments, 900°C has been chosen.

3. Determination of ternary tie-lines at the chosen solution treatment temperatures (in the present case, 900°C).

4. Preparation, solution treatment, and quenching of a series of metastable β alloys which will be very close to the β compositions available in two-phase alloys at this solution temperature (Row A, Figure 1).

5. Determination of the ageing response curves of these alloys at two or three reasonable ageing temperatures (in the present case, 550°C, 575°C and 600°C).

6. Ageing of each of these alloys to an equivalent point on their respective ageing curves.

7. Room-temperature mechanical testing of these aged β alloys, and choice of the strongest with reasonable ductility.

8. Preparation, solution treating, ageing and testing of a series of alloys containing this "best β" but having different proportions of equilibrium α (Row C of Figure 1). In this series of alloys the β will always be of composition N and the α of composition M; only the proportion will be changed.

An examination of the test results on the last mentioned series of alloys should reveal the optimum amount of α addition to the "best β".

It appeared probable that the choice of the "best β" by the above method would be complicated by brittleness in the aged β alloys. For this reason, a second group of alloys, similar to those in 4 above, were prepared. These alloys (Row B Figure 1) had a small percentage of primary α present in the β and it was hoped that this would impart a measure of ductility to the alloys to allow their full strength to be developed in a tensile test.

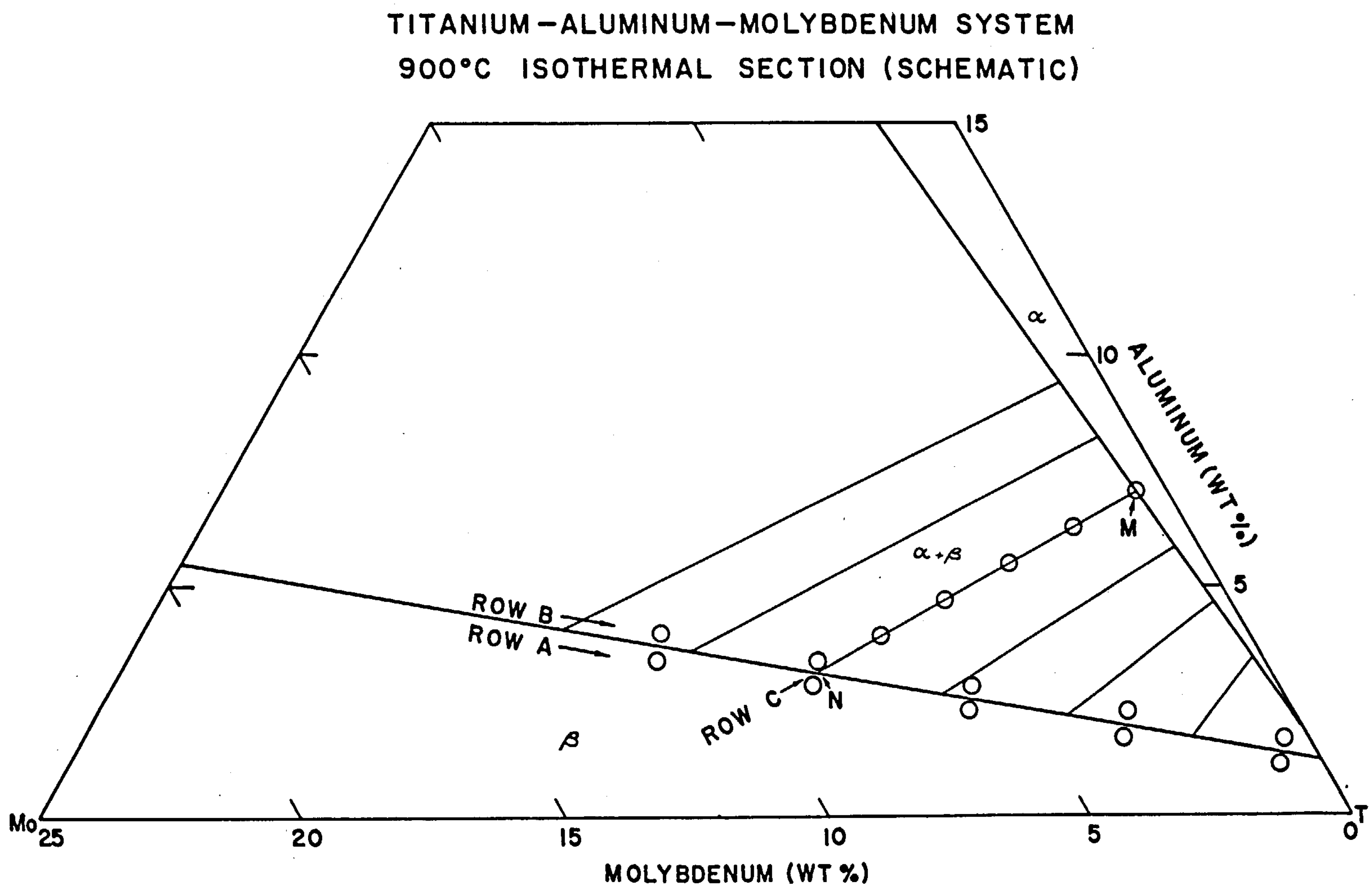

Fig. 1. - Schematic 900°C Isothermal Section of the Titanium-Aluminum-Molybdenum System.

EXPERIMENTAL

Alloy Preparation

Two groups of alloys were prepared for this investigation, constitutional alloys and experimental alloys. The first group, that for the determination of the 900°C isothermal section of the constitutional diagram, was made from iodide titanium, 99.9+% pure aluminum and high-purity sintered molybdenum powder. The second group, experimental alloys to be used for mechanical testing, was made from the same aluminum and molybdenum but was based on 106 BHN sponge.

Constitutional alloy ingots were all approximately 15 g in weight. Their composition was controlled by discarding all ingots which gained or lost more than 10 mg during melting. This resulted in nominal compositions of the alloys being accurate to better than ±0.1%.

To allow this system of control to be used with the experimental alloys, which were sponge based, the sponge was melted before weighing to preclude the relatively large melting losses which would be associated with it during alloying. These alloys, which weighed approximately 40 g each, were discarded if melting losses exceeded 15 mg. Thus their nominal compositions were also accurate to better than 0.1%.

The alloys were melted in a cold-hearth tungsten electrode arc furnace, the hearth of which had a V-shaped groove at the bottom to shape the melt. This V-shaped bottom produced an elongated cylindrical ingot about half an inch in diameter which was ideal for swaging. The ingots were homogenized by remelting four times with the ingot being placed at right angles to the "V" bottom of the crucible each time, after the method of Suiter[1].

Nearly all the ingots were then hot-swaged to 0.280 in. diameter rods and were stress-relieved at the swaging temperature. The four low-molybdenum alloys containing 10 to 12% aluminum were swaged at 900°C, and the four alloys on the 75% titanium section were used in the "as cast" condition. All other alloys were swaged at 850°C. After swaging, scale was removed from the bars by grit blasting and filing.

Metallography

For metallographic examination, all alloys were prepared by electro-polishing, using an electrolyte of 6% perchloric acid in glacial acetic acid and a current density of approximately 50 amp/dm^2 for two minutes.

For etching, the "R-etch" described by Ence[2] was used. The composition of this etchant is as follows:

19.5 g	benzalkonium chloride
35 ml	ethanol
40 ml	glycerine
25 ml	HF (50%).

This etch proved to be well suited for the point counting that was done for tie-line determinations, because it defined the structural boundaries very clearly without causing severe level differences between α and β.

Constitutional Diagram

Since it is the function of this work to deal with practical heat treatments, it was decided to determine the constitution of the alloy system based on a practical heat treating time rather than to attempt to develop true equilibrium data. In the following constitutional work, therefore, all alloys were annealed for four hours. Likewise, the experimental alloys were all solution treated for four hours to correspond with the constitutional diagram.

1. The $\beta / \alpha + \beta$ Boundary -

Two methods of determining points on the $\beta / \alpha+\beta$ transus of the constitutional diagram were used. In the first method, that of temperature brackets(3), the $\beta / \alpha + \beta$ transus temperatures of a number of alloys on the 75%, 91% and 95% titanium sections were determined to an accuracy of $\pm$ 3°C. These data were plotted on the constant titanium sections and were used to determine the composition at which the transus temperature was 900°C. Figure 2 is an example. In the second method, that of composition brackets, the β transus on the 900°C isothermal section was straddled by a number of alloys on the 82.5 and 88% titanium sections. These alloys were vacuum-annealed for four hours at 900°C $\pm$ 1°C, oil quenched, and examined metallographically for the presence of primary α in the $\alpha' + \beta$ matrix. These alloys may be seen in Figure 3.

Annealing and quenching of these alloys was carried out

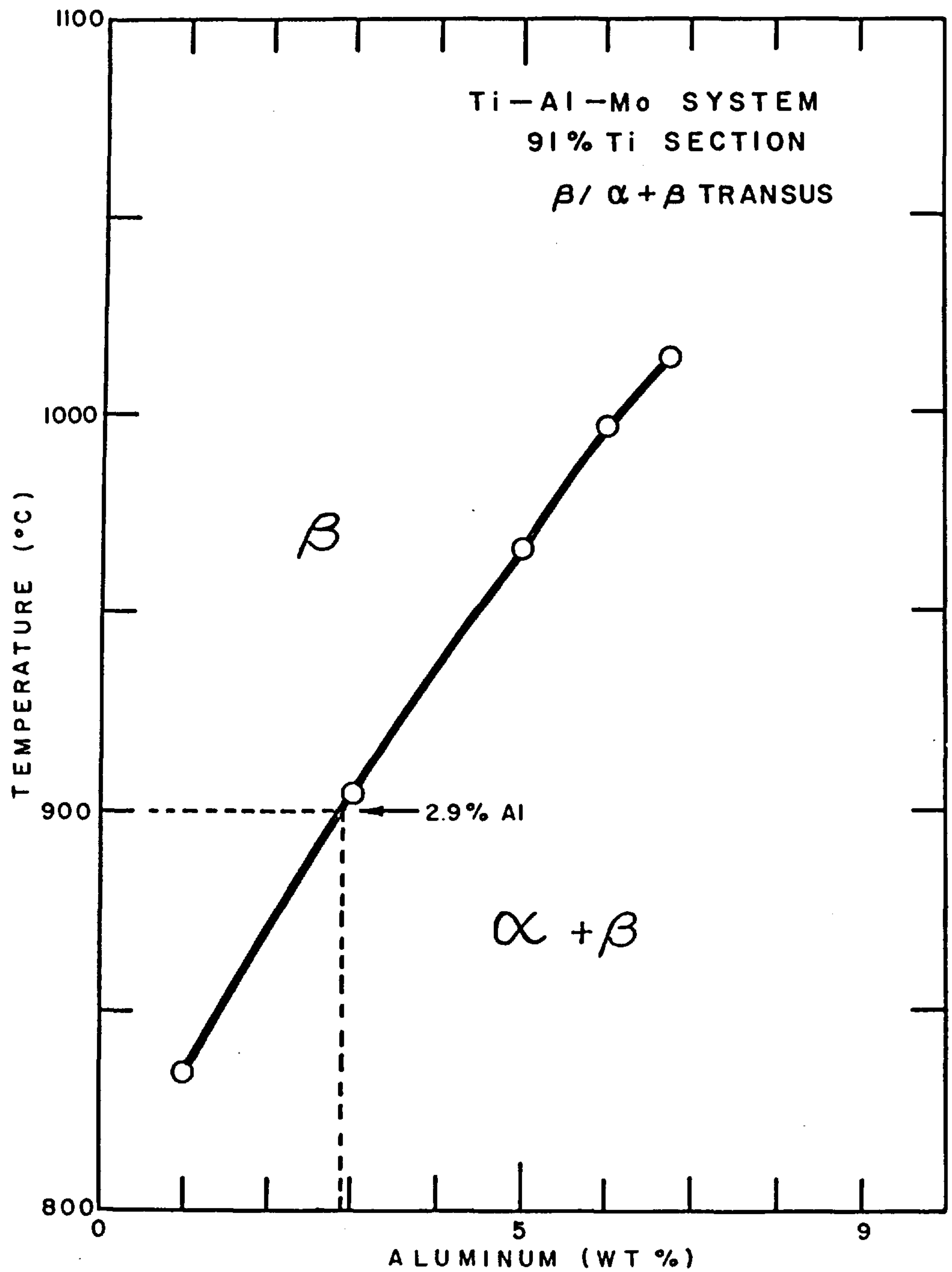

Fig. 2. - 91% Titanium Section of the Titanium-Aluminum-Molybdenum System.

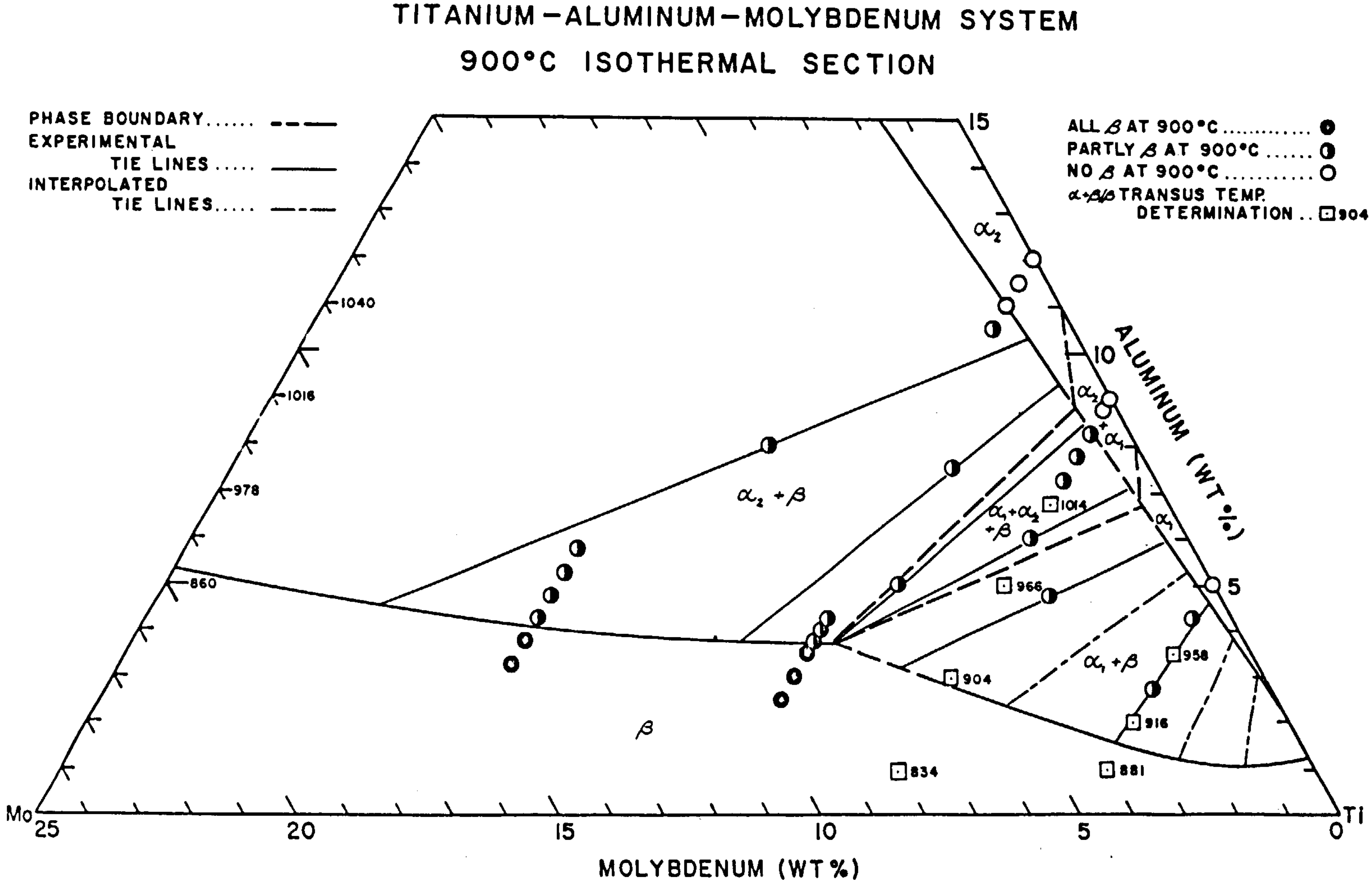

Fig. 3. - Experimentally Determined 900°C Isothermal Section of the Titanium-Aluminum-Molybdenum System.

in a vertical vacuum-quenching furnace similar to that described by Bennett[4]. This furnace was equipped with a saturable reactor temperature control system that enabled the temperature to be controlled to within $\pm$ 1°C over the range 700°C to 1100°C.

The data thus obtained were plotted and the 900°C $\beta / \alpha+\beta$ boundary drawn in (Figure 3).

2. <u>The $\alpha / \alpha+\beta$ Boundary</u> -

The $\alpha / \alpha + \beta$ boundary of the 900°C isothermal section was determined by the composition bracket method. Groups of alloys on the 88%, 91% and 95% titanium sections were vacuum annealed at 900°C $\pm$ 1°C, quenched and examined metallographically for the presence of β in the α matrix. These alloys, together with the $\alpha / \alpha + \beta$ boundary, are also shown in Figure 3.

3. <u>Ternary Tie-Lines</u> -

The six alloy compositions prepared for the determination of the tie-lines in the $\alpha + \beta$ region are shown in Table 1 and Figure 3. These alloys were vacuum annealed at 900°C and oil quenched. Longitudinal sections were polished, etched, and photographed. Photographs were taken of four different areas of each sample at a magnification of about X800. During printing, a reduced millimetre grid was superimposed on each print to enable a point count to be made of the phases in each photograph (Figure 4).

A square area slightly greater than 9 cm to a side was marked out on each photograph to include ten heavy centimetre lines

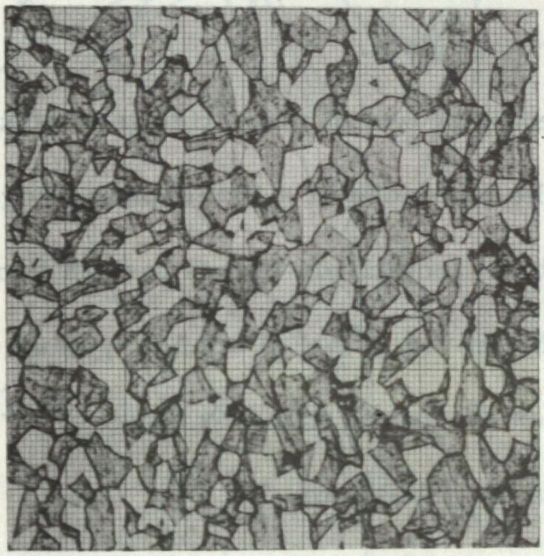

Fig. 4. - Photomicrograph of Ti-Al-Mo alloy, annealed 4 hr at 900°C and oil quenched. A grid is superimposed for point counting. The light etching phase is α. (X800, 'R' etch(2)).

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in each direction. Two counts were made along each of the centimetre lines in both directions, both forward and backward, resulting in 91 x 10 x 4 = 3640 intersections being examined on each print, or 14,560 intersections per alloy. From this examination, primary α percentages were worked out. The tie-lines were determined graphically from the primary α percentages and are shown in Figure 3, together with the other data.

The meeting of two of these tie-lines on the $\beta / \alpha + \beta$ boundary indicated the presence of a three-phase region ($\alpha_1 + \alpha_2 + \beta$) and this region has been tentatively drawn in with broken lines. The corners of this region on the $\alpha / \alpha + \beta$ boundary have been joined to the $\alpha_1 + \alpha_2$ boundaries that were found by Sagel et al[5] in the titanium-aluminum binary diagram.

Experimental Alloys

The experimental alloys prepared are listed in Table 2 and shown in Figure 5. Alloys B1 to B6, inclusive, are all -β alloys at the solution temperature (900°C) and alloys B7 to B12 inclusive are nearly all -β at the solution temperature containing less than 5%α. Figure 6 shows typical structures of equivalent alloys B3 and B9 situated opposite each other on either side of the $\beta / \alpha + \beta$ boundary.

Alloys B13 to B18, inclusive, since they are situated on a single tie-line, all have a single β composition (approximately that of B4) and a single α composition. The proportions of primary α in these alloys are 10, 20, 30, 50, 70 and 90% respectively.

TITANIUM – ALUMINUM – MOLYBDENUM SYSTEM
900°C ISOTHERMAL SECTION
SHOWING MECHANICALLY TESTED ALLOYS B1 – B18

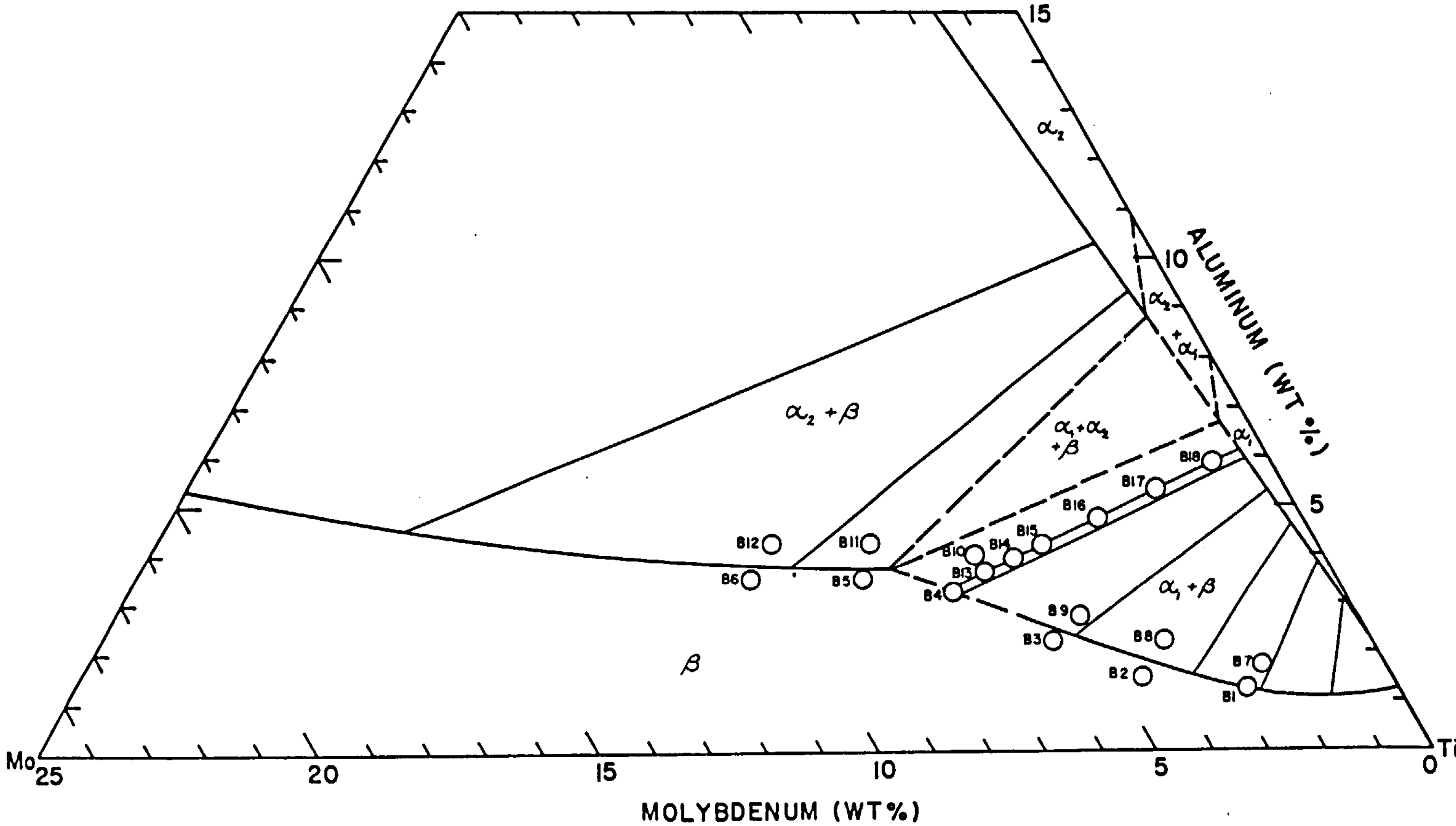
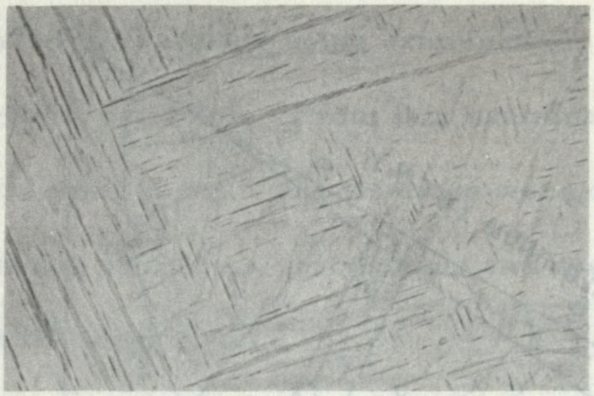
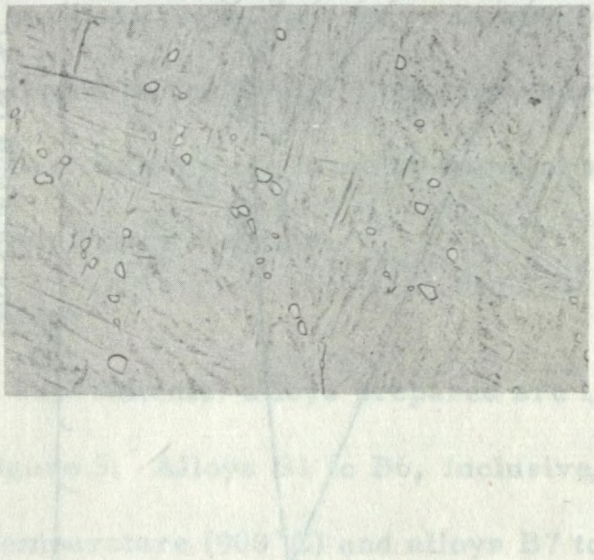


Fig. 5. - Experimentally Determined 900°C Isothermal Section of the Titanium-Aluminum-Molybdenum System, Showing Mechanically Tested Alloys B1-B18.



(a)

Alloy B3



(b)

Alloy B9

Fig. 6. - Photomicrographs of experimental Ti-Al-Mo alloys B3 and B9, solution treated 4 hr at 900°C and brine quenched. (X500, 'R' etch[2]).

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1. Ageing Response -

The ageing response of alloys B1 to B6 was determined after solution treatment at 900°C for 4 hr followed by brine quenching. Samples of these alloys were aged at three different temperatures, 550°C, 575°C and 600°C, and the hardness was determined at intervals from 15 minutes to 25 hr. The results of these ageing experiments are presented in Figure 7.

With the exception of B1, which showed little response to ageing, the alloys showed a hardness peak reached in 15 to 30 minutes, followed by a more or less gradual softening. In the case of ageing at 550°C, the softening process appeared to be interrupted by a levelling off or slight increase in hardness in the period 2 to 10 hours. This was followed by a continuation of the softening. Since high strength was the main criterion used in this work, the 550°C ageing temperature and the time of the start of the plateau were chosen for subsequent work. Thus, the ageing time for B1, B2, B3 and B4 was 2 hours and for B5 and B6, 4 hours.

2. Mechanical Testing -

(i) The all-β alloys

The two groups of alloys B1 to B6 and B7 to B12 were heat treated according to the above findings and mechanically tested on a Hounsfield Tensometer. The results of the tests are shown in Table 3, the properties shown being the average of three tests.

Only B1 of the first group and B7 and B8 of the second

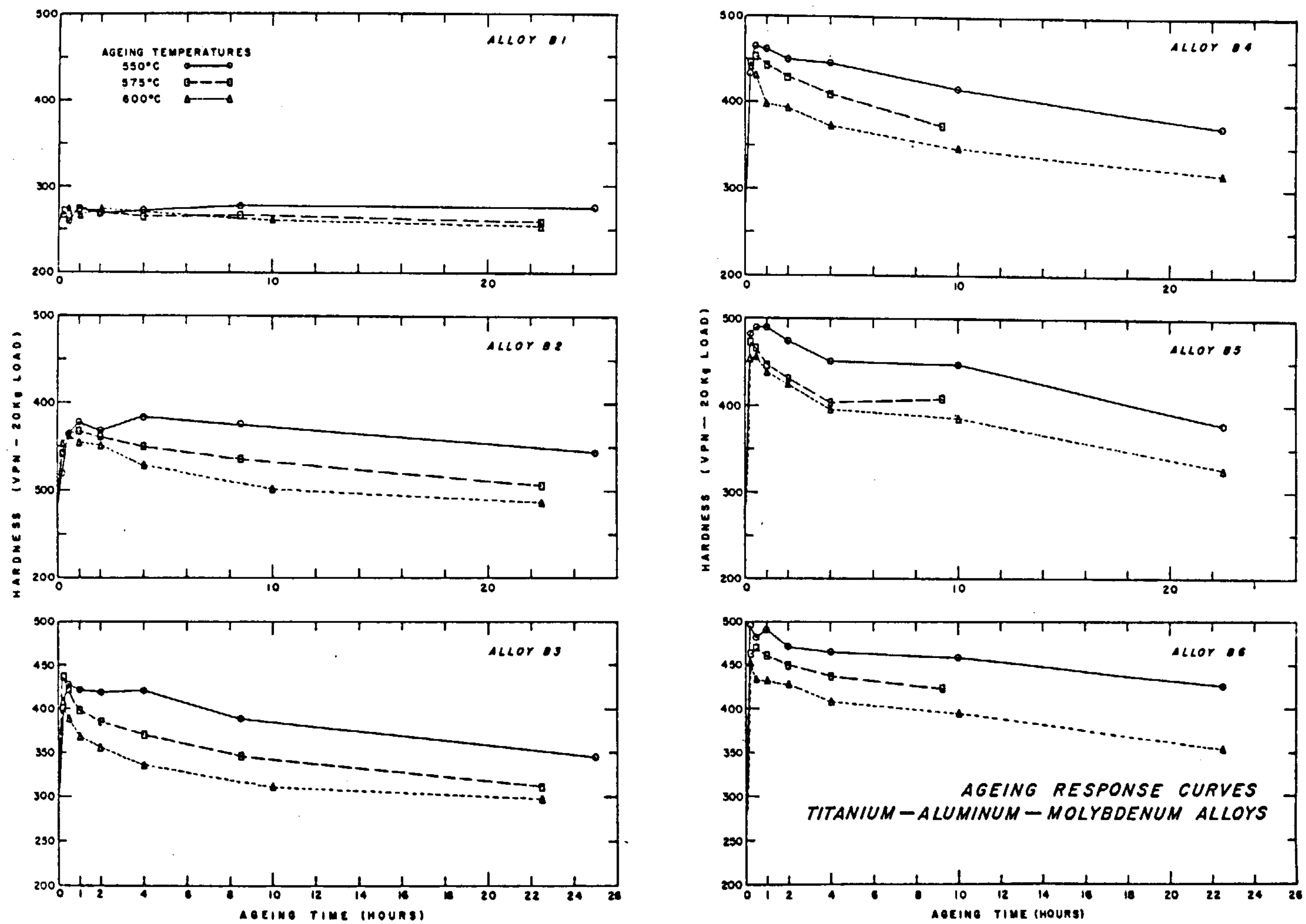


Fig. 7. - Ageing Response Curves of Experimental Ti-Al-Mo Alloys B 1 to B 6.

group show any appreciable measure of ductility. For this reason it appears that no choice of a "best β" can be made on the basis of these tests and that a greater proportion of α will have to be present to allow such a "best β" to be chosen by this criterion. Alloy B4 has, as a result, been chosen arbitrarily to represent a "best β" on which to base a series of α + β alloys for further testing.

(ii) The α + β alloys

The α + β alloys B13 to B18 were given heat treatments identical with that of B4 (solution treatment at 900°C for 4 hours, followed by brine quenching and ageing at 550°C for 2 hours). Mechanical testing was again carried out on a Hounsfield Tensometer.

The results of these tests are shown in Table 4 and are plotted with respect to primary α percentage in Figure 8, the properties shown being the average of three tests. The structure after ageing of three of these alloys B14, B16 and B17 is shown in Figure 9.

DISCUSSION OF RESULTS

Constitutional Diagram

The most obvious difference between the 900°C isothermal section shown in Figure 3 and that which can be derived from previous data[6, 7] is the presence, in the former, of a three-phase field. This is indicated by the crossing of two of the experimentally determined tie-lines near the β / α + β boundary and the change in direction of this boundary. The presence of such a three-phase field cannot be called unexpected, since Sagel et al[5] have reported the

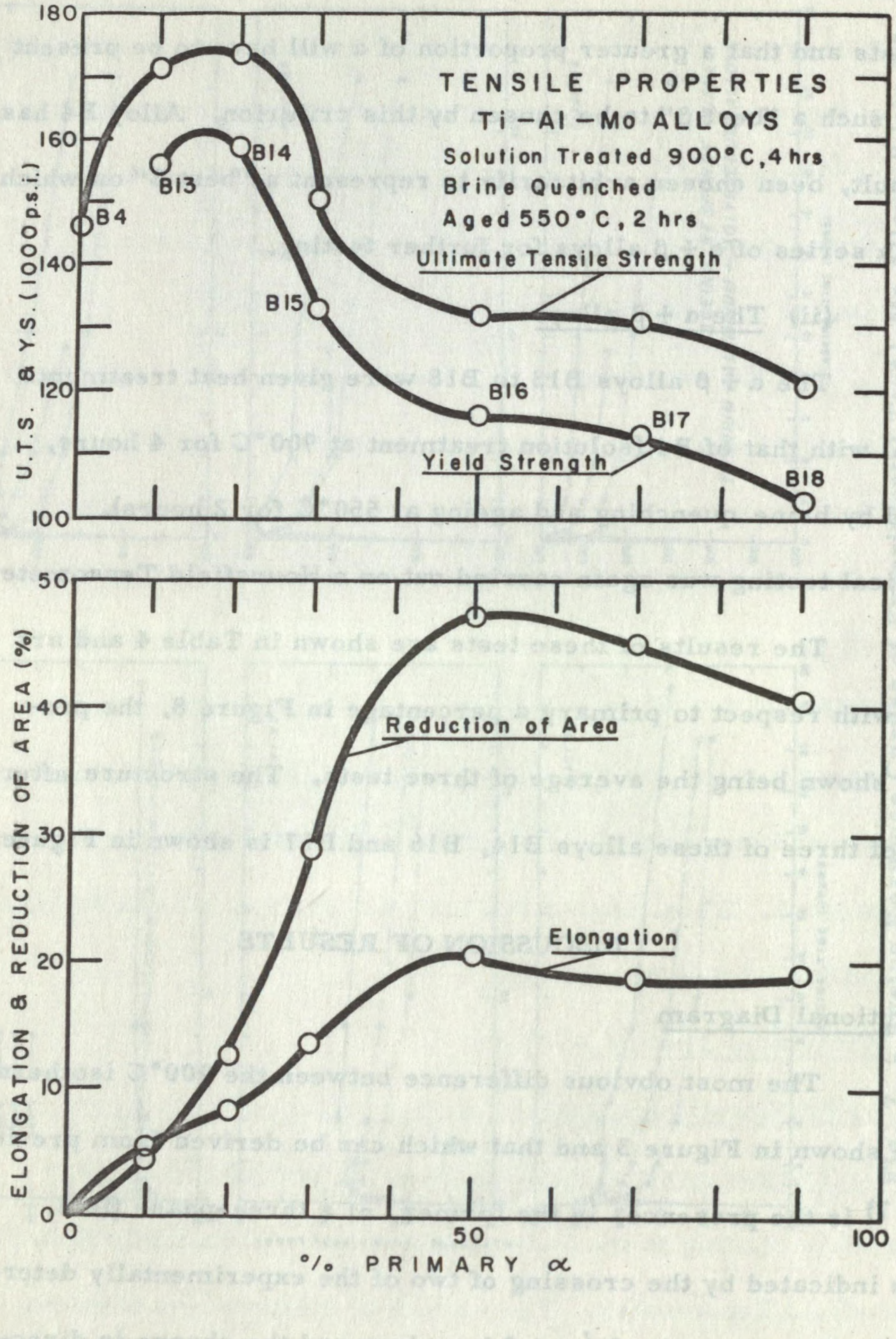
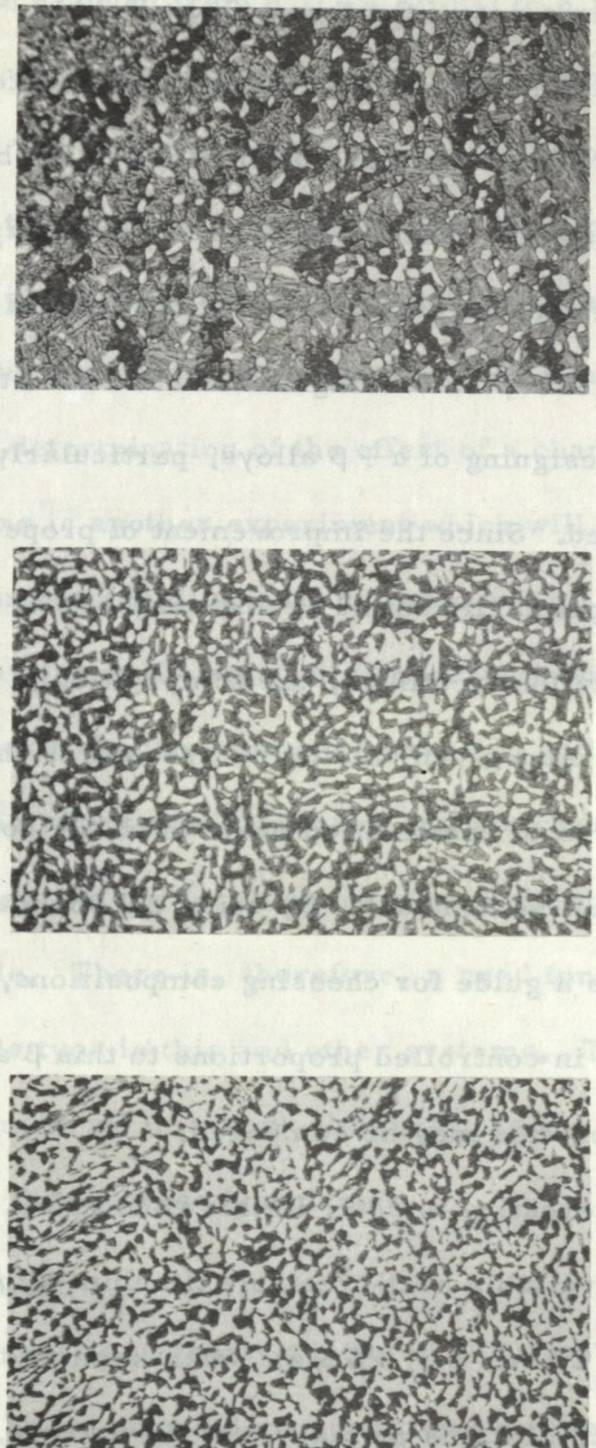


Fig. 8. - Tensile Properties of Experimental Ti-Al-Mo Alloys B4 and B13-B18.



(a)
Alloy B14,
= 20% primary α

(b)
Alloy B16,
= 50% primary α

(c)
Alloy B17,
= 70% primary α

Fig. 9. - Photomicrographs of experimental Ti -Al-Mo alloys B14, B16 and B17, solution treated 4 hr at 900°C and aged 2 hr at 550°C. (X500, 'R' etch[2]).

presence of a two-phase field, $\alpha_1 + \alpha_2$, in the Ti-Al binary system.

The boundaries of the three-phase field ($\alpha_1 + \alpha_2 + \beta$) have been drawn-in tentatively with broken lines, and the intersections of these lines with the α boundary have been joined to the binary boundary points found by Sagel. The latter lines define the $\alpha_1 + \alpha_2$ field.

The presence of such a three-phase field in Ti-Al-X systems in which X is a β stabilizing element is bound to be of great importance in the designing of $\alpha + \beta$ alloys, particularly where heat treatment is involved. Since the improvement of properties by heat treatment depends primarily on the ageing response of the β-phase produced during solution treatment, the composition of this β is of major importance. At a given solution temperature, this three-phase field provides an area of composition over which the composition of the β in any alloy will be constant. By using the boundaries of the three-phase field as a guide for choosing compositions, either α_1 or α_2 may be added in controlled proportions to this β and the resulting alloy properties may be compared.

It is interesting to note, in this connection, that one of the commercially available heat-treatable titanium alloys,(Rem-Cru C130A Mo(6 1/2% Al, 3 3/4% Mo), when solution treated at 900°C and quenched, contains primary α of the α_2 type, since it lies near the $\beta + \alpha_2$ boundary of this three-phase field. This means that the composition of the alloy could be changed without altering either proportion or composition of the β, by shifting the alloy to an equivalent point on the $\beta + \alpha_1$ boundary of the three-phase field. Thus, by reducing the aluminum content of the alloy by 1%, the composition of the α would be changed from 8 3/4% Al (α_2) to 6 3/4 Al (α_1) approximately, while the composition and proportion of β would remain constant. The effect of such a change on the properties of the alloy after heat treatment are not known yet, but a gain in ductility appears to be a possibility. However, such an experiment will have to await the accurate determination of the three-phase field boundaries.

The determination of the effect of a change in solution treatment temperature is another experiment which will have to await the completion of further constitutional diagram work. While it is evident that a raising of the solution temperature will increase the aluminum content of the β-phase and a lowering will have the opposite effect, the way in which a solution temperature change will affect the tie-line directions and the location and size of the three-phase field is not predictable. There is, therefore, a need for more constitutional data of this type in this and other systems. The outstanding technical problem in all this work, however, is the accurate determinations of the three-phase boundaries.

Experimental Alloys

The tensile property graphs of Figure 8 show that the series of alloys based on the β-composition B4 reach a maximum tensile strength at an α-content of about 20%, after which the strength falls off rapidly, levelling off at about 50% α. On the other hand, the ductility increases steadily from 0 to 50% α before levelling off.

Consequently, in this group of alloys, those containing 20 to 50% α show a useful range of properties which could well serve as a basis for the choice of an alloy composition for a specific application.

When the α-content is over 50%, the properties of the alloy are approximately those of the α-phase alone. It can, therefore, be seen that there is little point in having this particular aged β in the structure unless there is more than 50% present.

One of the original objects of the present work, that of selecting a "best β" composition, has not yet been achieved. However, the tensile properties of the series of alloys B13 to B18 suggest that it might be possible to choose such a "best β" on the basis of the properties of a series of alloys such as B1 to B6 with 10-20% α added. Moreover, these results indicate that the type of approach to heat-treatable alloy design adopted in this work could be very useful in producing data on which to base the design of heat-treatable α + β titanium alloys having specific properties.

SUMMARY

1. The titanium-rich corner of the 900°C isothermal section of the Ti-Al-Mo constitutional diagram has been re-determined, based on a 4-hour annealing time, and ternary tie-lines have been added. The presence of a three-phase field, $\alpha_1 + \alpha_2 + \beta$, has been indicated.

2. A system for the design of heat-treatable Ti-Al-Mo alloys, based on this isothermal section, is being examined. This

system is based on the choosing of the best β composition available on solution treatment at 900°C, and the addition to it of controlled amounts of α of a fixed composition.

3. First indications are that tensile test results on all-β alloys close to the β / α + β boundary do not form a good basis for choosing the best β on which to base a high-strength alloy, because of the brittleness of aged β alloys in this composition range. In one case it was necessary to add 10-20% α to a given β to produce sufficient ductility for the full tensile strength to be realized in a test.

4. In one experiment, the addition of controlled amounts of α of a fixed composition to a given β resulted in a maximum tensile strength being reached at 20% α, after which the strength fell off to reach an almost constant low level at 50% α and beyond. The ductility increased steadily from 0 to 50% α, after which it levelled off.

ACKNOWLEDGMENT

The author is indebted to Mr. H. V. Kinsey, head of the Refractory Metals Section of the Physical Metallurgy Division, for many helpful discussions during the course of this project, which was carried out under his general direction, and to the staff of the Refractory Metals Section generally for their assistance in the experimental work.

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(Tables 1 to 4 follow,)
(on pages 25 and 26.)

TABLE 1

Percentage of Primary α at 900°C in Alloys for Tie-Line Determinations

Alloy Composition Al (wt. %)	Mo (wt. %)	Primary α (%)
2.75	2.25	40.3
6.00	3.00	69.1
4.75	3.25	54.8
7.50	3.75	67.3
5.00	6.00	28.0
8.00	7.00	60.7

TABLE 2

Experimental Alloy Compositions

Alloy No.	Composition Al (wt %)	Mo (wt %)	Alloy No.	Composition Al (wt %)	Mo (wt %)
B1	1.25	2.75	B10	4.00	6.25
B2	1.50	4.50	B11	4.25	8.00
B3	2.25	5.75	B12	4.25	9.75
B4	3.25	7.00	B13	3.70	6.25
B5	3.50	8.50	B14	3.90	5.60
B6	3.50	10.50	B15	4.20	4.95
B7	1.75	2.25	B16	4.75	3.65
B8	2.25	3.75	B17	5.30	2.35
B9	2.75	5.00	B18	5.90	1.10

TABLE 3

Tensile Properties of Alloys B1-B12 After Heat Treatment
(Sol. tr. 4 hr at 900°C, brine quenched, aged at 550°C)

Alloy No.	Ultimate Tensile Strength (psi)	Yield Strength (psi)	Elongation (%)	Reduction of Area (%)
B1	117,200	104,400	17	43
B2	158,100	-	-	-
B3	151,700	-	-	-
B4	148,300	-	-	-
B5	168,900	-	-	-
B6	124,600	-	-	-
B7	119,700	103,800	22	66
B8	133,800	118,100	12	32
B9	172,200	-	-	-
B10	189,900	-	-	-
B11	161,100	-	-	-
B12	128,100	-	-	-

TABLE 4

Tensile Properties of Alloys B13-B18 After Heat Treatment
(Sol. tr. 4 hr at 900°C, brine quenched, aged 2 hr,at 550°C)

Alloy No.	Ultimate Tensile Strength (psi)	Yield Strength (psi)	Elongation (%)	Reduction of Area (%)
B13	171,800	156,400	6	4
B14	173,200	158,900	8	15
B15	150,800	133,100	14	29
B16	132,000	116,100	20	48
B17	131,200	113,200	19	45
B18	120,300	102,500	19	40

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